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Variation of O^{18} content of waters from natural sources

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ABSTRACT

A number of marine water and fresh water samples were examined for the relative O^{18}/O^{16} ratio, and the variation of this ratio was determined to a precision of $\pm 0{\cdot}1‰$. In the case of surface marine waters, for a range of salinity of 29–40‰, the O^{18} content varies over a range of approximately 6‰. The low O^{18}/O^{16} ratios were obtained from surface marine waters contaminated with meltwater from the ice fields, while the marine waters of high salinity were richest in O^{18}. The observed relation between O^{18} content and salinity of the oceanic waters can be explained by a process of multiple stage distillation which produces a continuous loss of fresh water to the ice regions from the surface waters of the warm oceans. The lower salinities of cold ocean currents, such as the Alaskan and Californian currents, are due primarily to mixing with meltwater from cold regions. The effect of glaciation upon the isotopic method of measuring paleotemperatures is discussed. The results for deep oceanic samples and for non-typical water samples are also discussed.

Introduction

The chemical elements forming the earth's crust have been subjected to much chemical processing during the past history of the earth and are now being so processed. The natures of these processes have attracted attention in many fields of study. The effect of isotopic compositions on thermodynamic properties of simple chemical compounds of the lighter elements, as first presented by Urey (1935), shows that isotopic fractionation accompanies many of these natural processes. Consequently, the present isotopic composition of the lighter elements should reflect how their present state was reached. For example, the variation of the isotopic composition of oxygen in natural waters on the surface of the earth should be mainly controlled by the processes of evaporation and condensation. Variations of the O^{18}/O^{16} ratio in natural waters have been demonstrated by Dole (1935), Thode (1949) and others who have analysed waters from the supersaline and highly evaporated Dead Sea, and from the Great Lakes and some glacier lakes.

In connection with work on paleotemperatures (Urey, 1948; Urey *et al.*, 1951; Epstein *et al.*, 1951) where precise measurements of the O^{18}/O^{16} ratio of oxygen in the $CaCO_3$ of marine shells relative to the same ratio in oxygen of the surrounding water is used as a measurement of temperature at which the animal grew, it was necessary to determine the variation of the O^{18}/O^{16} ratio in the normal marine waters. The variations of the O^{18} concentration in normal marine waters proved to be about ten times greater than the variation produced by a 1°C change of temperature on the O^{18} concentration in the $CaCO_3$. If such variations existed in the oceans of the past, they would introduce considerable error in measurements of paleotemperatures. This relatively large variation and the ability to measure the O^{18}/O^{16} ratio with precisions greater than reported by other workers stimulated the writers to investigate additional water samples including some from other than the usual marine sources. The hope was to obtain relevant information

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regarding the processes that contribute to the O^{18}/O^{16} heterogeneity in natural waters.

Samples

Most of the samples off the west coast of North America were furnished by Dr. N. W. Rakestraw of the Scripps Institution of Oceanography. The samples around the equatorial belt were submitted by Dr. H. Pettersson who collected them during the Albatross Expedition (1949). Salinity data accompanied these samples. Other samples were contributed by Dr. R. Buchsbaum, Dr. H. A. Lowenstam, Dr. R. Bader, Mr. G. Snyder and Dr. R. Ginsburg. Salinities of these latter samples were determined in this laboratory by the well-known silver nitrate titration method.

Experimental

The experimental procedure used in determining the relative O^{18} concentration of waters consists essentially of equilibrating approximately 175 cc (N.T.P.) of carbon dioxide gas with 25 g of water in a thermostated bath and then analyzing about a 3 cc aliquot of the gas in a mass spectrometer. In detail, the procedure is as follows: the pH of the ocean sample is adjusted to 6 or lower to facilitate more rapid equilibration (Mills and Urey, 1940). The sample is inserted into a 200 cc round bottom flask provided with ground glass joints. A stopcock is attached and the assembly connected to a vacuum manifold. The water is frozen in a solid carbon dioxide-chloroform-carbon tetrachloride bath and the air quickly pumped away. The ice is melted and warmed to room temperature to release gas which was trapped during the initial freezing. The water is then refrozen and pumped for a minute to remove the remaining non-condenlsibe gases. The ice is melted again and commercial cylinder carbon dioxide introduced into the flask to a pressure about 2 cm less than atmospheric. After equilibration in a bath thermostated at 25·3°C for three days, a 3 cc aliquot of carbon dioxide is withdrawn by means of a gas pipette system and analyzed in the mass spectrometer using the method described by McKinney *et al.* (1950). Aliquots of gas are withdrawn at two day intervals and analyzed until a constant value for the relative O^{18} content is obtained. The flask is frequently shaken during equilibration to insure that water deficient in O^{18} is not condensed on the walls of the vessel. The water level of the bath is always kept just above the stopcock to prevent cooling of the vessel and to minimize condensation of the lighter vapour on the vessel walls. Usually analyses of 3 or 4 aliquots taken at successive times were sufficient to demonstrate that equilibrium was attained.

The mass spectrometer analyses as reported here are relative to a standard carbon dioxide gas. This is the product of a reaction between 100% phosphoric acid and a certain quantity of a powdered large belemnite from the Peedee formation of North Carolina. The analyses are calculated from the formula

$$\delta = 1000 \left[\frac{R_{\text{sample}}}{R_{\text{standard}}} - 1 \right]$$

where R is the ratio of masses 46 and 44 and δ represents the deviation of the

concentration of O^{18} of the sample from that of the standard in per mil, with a probable error of $\pm 0{\cdot}1‰$.

Since the cylinder carbon dioxide analyzes $-17‰$ relative to carbon dioxide equilibrated with an average ocean sample, the δ's of a series of aliquots from a single flask approach a maximum. Earlier analyses of some of the present samples were reported in a previous publication (Epstein *et al.*, 1951), and those analyses are in general anywhere from 0·2 to $-0{\cdot}7‰$ relative to the ones which have been subsequently repeated. These discrepancies were due to incomplete equilibration of the previous samples. This error is not serious since it does not change any of the conclusions drawn at the time except the mean value of δ for ocean water.

The present results are listed in Table 1. Section 1 includes samples collected in marine systems of currents not likely to be contaminated with water from melted ice; Section 2 includes marine samples collected from other areas; and Section 3 includes fresh water samples. Column 1 contains sample numbers; Column 2, the locations of the samples; Column 3, the salinities; Column 4, the depths; Column 5, the analyses obtained from the last two or three aliquots of gas; and the last column lists the averages of the numbers in Column 5.

Discussion

The average isotopic composition of oxygen of ocean waters

For the purpose of determining a mean value of δ for ocean water, an average was taken of the isotopic ratio data of all samples ranging in depth between 500 and 2000 metres. The average salinity for this group of samples was 34·7 and $\delta = -0{\cdot}04 \pm 0{\cdot}1‰$. For convenience, mean δ of ocean water was taken to be 0·00 with an average deviation of $\pm 0{\cdot}1$. The uncertainty that this is the true mean value of ocean water is probably greater than indicated because of the limited number of samples used.

Relationship between salinity and O^{18} content of ocean waters

On examination of the data of Table 1, Sections 1 and 2, a correlation between salinity and O^{18} content of ocean waters is immediately obvious (Fig. 1, Curve I). Generally the processes which affect the O^{18} content of the oceans tend to change the salinity in a similar manner. However, this similarity is only qualitative, as it can be understood on examining the relative O^{18}/O^{16} ratio analyses for some typical fresh water sources (Table 1, Section 3). Addition of fresh water from melted snow ($\delta = -17{\cdot}0$) will decrease the O^{18} content of ocean waters approximately 3·5 times as much as the addition of an equal amount of fresh water from the mouth of the Mississippi River ($\delta = -4{\cdot}9$). Thus ocean waters of the same salinity can have a different O^{18} content. The approximate linearity in the relationship shown by Fig. 1 is enhanced by the fact that the majority of the samples of salinities 34·5 and lower have been collected in the Alaska and California currents along the west coast of North America where melting snow and ice play a major role in lowering salinity. Clearly, the more constant the isotopic composition of the fresh water contaminant, the more probable will be the linear relationship between salinity and the O^{18} content of ocean waters. Fig. 2 is based

Table 1. *Relative* O^{18} *content of waters from natural sources*
Section 1. *Samples in marine system of currents that cannot directly be contaminated with meltwater*

Sample No.	*Location*	*Salinity* ‰	*Depth* (m)	δ (*as measured*)		δ (*mean*)
1	N 30°47′ W 25°25′	37·4	10	0·93	0·88	0·90
2	N 30°47′ W 25°25′	35·4	1000	0·03	0·06	0·05
3	N 26°25′ W 34°00′	34·9	5000	−0·30	−0·26	−0·28
				−0·28		
4	N 14°27′ W 66°13′	34·9	5000	−0·23	−0·11	−0·21
				−0·30		
5	N 14°15′ W 71°02′	36·0	0	0·94	0·91	0·92
6	S 02°52′ W 88°20′	34·4	20	−0·09	−0·09	−0·09
7	S 02°52′ W 88°20′	34·6	1000	−0·30	−0·38	−0·34
8	S 13°25′ W 149°30′	35·8	0	0·32	0·36	0·34
9	S 13°25′ W 149°30′	34·6	1000	−0·26	−0·15	−0·20
10	S 13°25′ W 149°30′	34·7	4000	−0·49	−0·44	−0·48
				−0·51		
11	S 07°45′ E 120°30′	34·5	10	0·74	0·80	0·78
				0·81		
12	S 07°45′ E 120°30′	34·6	1000	−0·38	−0·34	−0·36
				−0·36		
13	N 10°06′ E 52°45′	35·5	20	0·23	0·31	0·27
14	N 10°06′ E 52°45′	35·0	500	−0·05	−0·08	−0·06
15	S 00°13′ W 18°26′	35·6	25	0·48	0·48	0·48
16	S 00°13′ W 18°26′	34·7	500	−0·20	−0·06	−0·13
17	S 00°13′ W 18°26′	34·9	2500	−0·22	−0·32	−0·27
18	S 00°13′ W 18°26′	34·8	7500	−0·50	−0·44	−0·47
19	N 28°05′ W 60°49′	36·8	25	1·02	0·89	0·96
20	N 28°05′ W 60°49′	36·3	500	0·49	0·48	0·48
21	N 28°05′ W 60°49′	35·0	2000	−0·06	−0·04	−0·05
22	N 28°05′ W 60°49′	34·9	6000	−0·14	−0·23	−0·18
23	N 43°04′ W 19°40′	35·9	25	0·29	0·39	0·34
24	N 43°04′ W 19°40′	35·0	2000	−0·06	0·03	−0·01
25	N 43°04′ W 19°40′	34·9	6000	−0·23	−0·22	−0·22
26	N 18°33′ W 120°42′	34·4	0	0·05	−0·03	0·01
27	N 18°33′ W 120°42′	34·6	1480	−0·11	−0·30	−0·21
28	N 03°50′ W 125°12′	34·4	0	0·24	0·20	0·22
29	N 03°50′ W 125°12′	34·6	710	0·11	−0·03	0·08
				0·15		
30	N 03°50′ W 125°12′	34·6	1075	−0·08	−0·21	−0·14
31	N 10°41′ W 126°15′	34·4	0	0·00	0·03	0·02
32	N 10°41′ W 126°15′	34·5	766	0·18	0·01	0·10
33	N 10°41′ W 126°15′	34·6	1507	−0·06	−0·07	−0·07
34	N 18°43′ W 139°20′	34·6	0	0·38	0·22	0·30
35	N 18°43′ W 139°20′	34·5	1291	0·11	−0·08	0·01
36	N 20°58′ W 150°19′	34·7	0	0·24	0·17	0·20
37	N 20°58′ W 150°19′	34·6	1541	−0·16	−0·25	−0·20
38	N 25°42′ W 160°20′	35·2	0	0·24	0·22	0·23
39	N 25°42′ W 160°20′	34·4	999	−0·06	−0·04	−0·05
40	N 25°42′ W 160°20′	34·6	1703	0·08	0·04	0·06
41	Bermuda (North of Island)	36·3	~0	0·99	0·91	0·95
42	Bermuda (Garnet Rock)	36·4	~0	0·80	0·88	0·84
43	Bermuda	36·8	~0	1·09	1·17	1·13

Table 1 (*continued*)

Sample No.	*Location*	*Salinity* ‰	*Depth* (m)	δ (*as measured*)		δ (*mean*)
44	Bermuda (Harrington Sound)	35·4	~0	0·82	0·77	0·80
45	Bermuda (Harrington Sound)	35·4	~18	0·86	0·82	0·84
46	Near mouth of Caesar Creek in Florida	36·4	~0	0·97	0·97	0·97
47	Off Jacksonville, Florida	35·7	~0	0·66	0·87	0·73
				0·65		
48	Near mouth of Oyster Creek in Florida	29·6	~0	3·37	3·60	3·49
49	Palau in-shore side of barrier reef	34·3	~0	0·07	0·17	0·12
50	Palau (between two islands)	33·8	~0	−0·23	−0·19	−0·21
51	Guam (Tumon Bay) (behind barrier)	34·5	~0	−0·03	0·11	0·01
				−0·06		
52	Guam (Tumon Bay) (outside barrier)	35·4	~0	0·17	0·10	0·13
53	Nagai Beach, Japan	33·0	~0	−0·44	−0·44	−0·44
54	Off Okino Shima, Japan	34·2	~0	0·00	−0·05	−0·02
55	Off Hawaiian Islands (Station 7)	34·6	~200	0·16	0·19	0·17
56	Gulf Stream off Norway	35·2	~0	0·16	0·11	0·13
57	West Lake (at Flamingo Road), Florida	28·3	~0	4·50		4·50
58	N 35°41′ E 21°50′	38·8	50	1·13	1·16	1·15
59	Mediterranean	38·7	2000	1·02	1·02	1·02
60	Off Saipan Island	40·2	~0	2·46	2·58	2·52
Section 2.	*Samples in marine systems of currents into which meltwater can flow*					
61	N 48°53′ W 135°00′	32·6	0	−1·33	−1·12	−1·22
62	N 48°53′ W 135°00′	34·1	602	−0·16	−0·20	−0·19
63	N 48°53′ W 135°00′	34·4	1205	−0·13	−0·04	−0·08
64	N 54°19′ W 137°03′	32·8	0	−0·85	−0·94	−0·90
65	N 59°24′ W 144°50′	32·6	0	−0·96	−0·89	−0·92
66	N 57°00′ W 150°00′	32·9	0	−0·99	−0·76	−0·95
				−1·11		
67	N 57°00′ W 150°00′	33·6	110	−0·19	−0·16	−0·17
68	N 57°00′ W 150°00′	34·0	321	−0·44	−0·42	−0·38
				−0·27		
69	N 58°05′ W 150°00′	33·8	0	−0·88	−0·99	−0·94
70	N 49°58′ W 146°30′	32·6	0	−1·10	−1·18	−1·14
71	N 39°41′ W 137°03′	33·3	0	−0·67	−0·68	−0·68
72	N 38°20′ W 132°29′	33·1	0	−1·08	−1·10	−1·09
73	N 44°20′ W 125°50′	32·1	0	−1·33	−1·18	−1·25
74	N 43°58′ W 133°15′	32·7	0	−0·97	−0·98	−0·97
75	N 26°17′ W 121°40′	34·0	0	−0·56	−0·50	−0·53
76	N 35°41′ W 121°50′	33·0	0	−0·80	−0·76	−0·78
77	N 33°19′ W 128°32′	33·5	0	−0·67	−0·81	−0·74
78	N 33°19′ W 128°32′	34·0	294	−0·29	−0·19	−0·24
79	N 33°19′ W 128°32′	34·5	1289	−0·16	−0·29	−0·19
				−0·12		

Table 1 (*continued*)

Sample No.	*Location*	*Salinity* ‰	*Depth* (m)	δ (*as measured*)		δ (*mean*)
80	N 28°18′ W 117°30′	33·7	0	−0·50	−0·38	−0·44
81	N 28°18′ W 117°30′	34·4	598	0·09	0·18	0·09
				0·00		
82	N 28°18′ W 117°30′	34·6	1512	−0·06	−0·03	−0·01
				+0·06		
83	Santa Tomas	33·6	0	−0·40	−0·40	−0·40
84	Pt. between Morro and Ensenada	33·8	0	−0·29	−0·27	−0·28
85	President Channel, Friday Harbour	31·2	171	−1·63	−1·60	−1·62
86	Middle Channel, Friday Harbour	33·2	157	−0·67	−0·59	−0·63
87	Monterey Bay, Pacific Grove	33·8	0	−0·41	−0·46	−0·44
88	La Jolla, California	33·9	0	−0·40	−0·49	−0·44
89	N 52°08′ W 176°54′	33·1	0	−0·89	−0·81	−0·85
90	Off shore of Greenland	16·2	0	−11·10	−11·05	−11·07
91	N 44°9′5″ W 68°14′6″	33·0	0	−0·99	−1·08	−1·04
92	Aleutians (Patterson Pt.)	33·2	0	−0·78	−0·84	−0·81
93	Greenland (East Coast)	29·3	0	−3·30	−3·39	−3·35
Section 3.	*Fresh water*					
94	Snow (Snowfall, Chicago, 12-14-51)			−17·08	−16·97	−17·02
95	Columbia River (Trail, B.C.)			−17·24	−17·65	−17·45
96	Rain (Bermuda)			−6·54	−6·55	−6·55
97	Mississippi River (St. Louis)			−8·93	−8·85	−8·89
98	Mississippi River (Baton Rouge)			−4·86	−4·92	−4·89
99	Lake Michigan			−6·15	−6·12	−6·13
100	Great Salt Lake	219·5		−7·38	−7·48	−7·44
101	Rain Water (Chicago)			−7·21	−7·03	−7·12
102	Condensate from fumarole: Parícutin			6·72	6·78	6·75
103	Water from air oxygen			22·24	21·95	22·10

on salinities and O^{18} analyses from samples of Section 2 exclusive of samples from depths greater than 1000 m. In this case a rather consistent relationship is apparent. If this relationship is assumed to be linear, the δ for the fresh water contaminant (of zero salinity) is −20‰. This value is in approximate agreement with that obtained for snow and Columbia River water collected at Trail, British Columbia, but is markedly different from the δ's obtained from fresh water of the Great Lakes, Chicago and Bermuda rain, and the Mississippi River. One can conclude that the large change of δ of ocean waters per unit of salinity for the samples considered above must be due primarily to dilution with meltwater from ice at high altitudes and high latitudes.

Fig. 3 is based on salinities and O^{18} analyses from samples of Section 1,

exclusive of samples from depths greater than 1000 m. In this case, where the samples are chiefly from regions with warm to temperate water, a scattering of points without much correlation is obtained. This type of plot probably approximates more closely the salinity to O^{18} relationship existing in the present oceans than does the more linear one shown in Fig. 2. Epstein, Friedman and Urey* have shown that for the liquid-vapour water system at 29°C, the liquid is 7‰

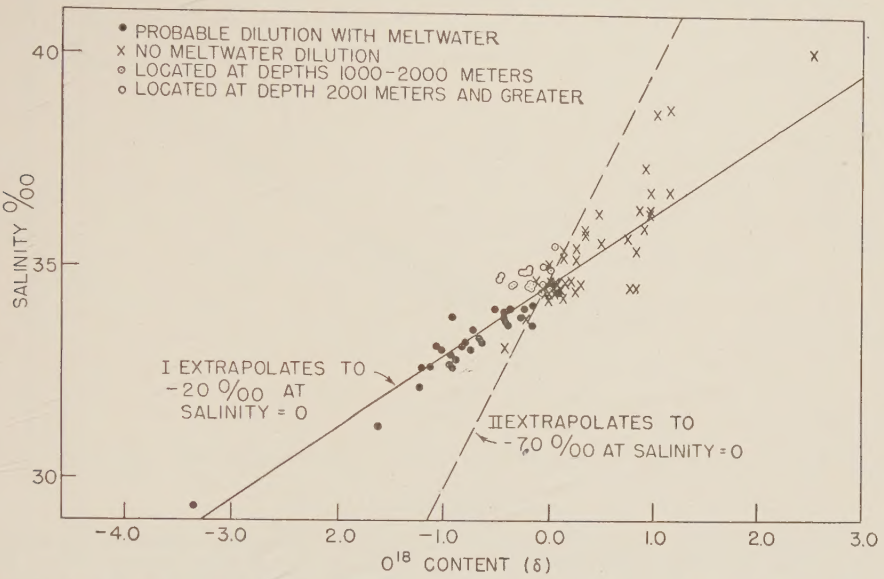

Fig. 1. Relation between salinity and O^{18} content of all ocean water samples studied, except a few of unusual isotopic composition.

Curve I. Same as that of Fig. 2, q.v.
Curve II. Calculated relationship that would exist between δ and salinity if the fresh water addition or depletion due to evaporation had a δ of ca.—7‰ relative to the mean value for ocean water.

richer in O^{18} than is the vapour phase. If the mixing layer of the ocean may be considered as such a system, evaporation changing salinity from 35‰ to 36‰ (loss of 2·8% of fresh water) should cause an increase of 0·2‰ in the O^{18} content. The dashed curve in Fig. 1 (Curve II) represents the calculated relationship between δ and salinity that would exist if the fresh water addition or depletion due to evaporation had a δ of approximately —7‰ relative to the mean value for ocean water. If in Table 1, Section 1 comparison is made between the data for surface samples and deep samples from the same location, the effect of evaporation and condensation on the change of O^{18} content with change in salinity should be obtained. For example, the decreases of salinity and O^{18} concentration between samples 1 and 2 are respectively 2·0 and 0·85‰ that is, a specific change in δ of 0·43‰ per unit of salinity. Similarly, comparison between samples 8 and 9 shows a specific decrease in δ of 0·45‰ and between samples 11 and 12 a decrease of 1·2‰ although in this latter case salinity is essentially the same. The majority of samples of Section 1 indicate a larger increase in O^{18} per unit of salinity change than can be expected

* Manuscript in preparation.

if increase of salinity were due to evaporation of fresh water analyzing —7‰ relative to the mean value for ocean water. This effect is shown by the points lying in the region of salinity greater than 35‰ in Fig. 1. These follow more closely the relationship between salinity and O^{18} content resulting from addition or depletion of water of δ equal to —20‰ as shown by Curve I. The points which deviate more

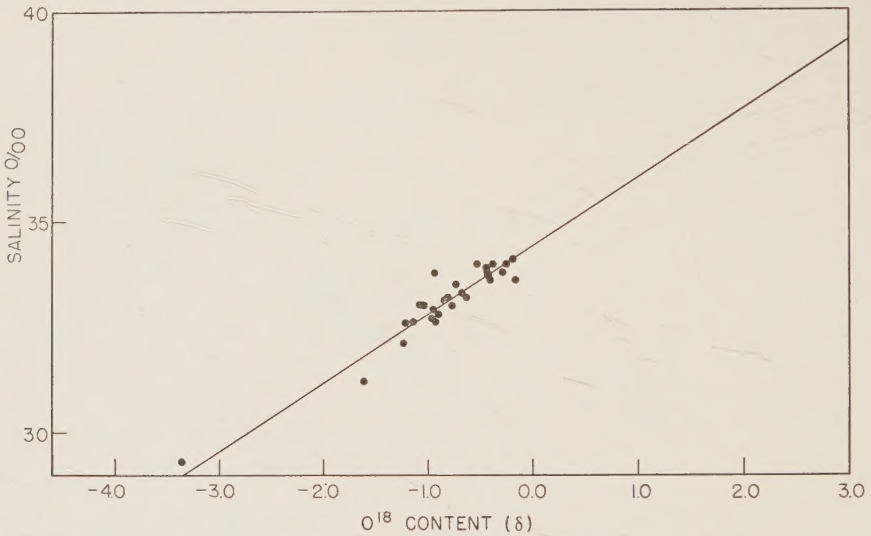

Fig. 2. Relation between salinity and O^{18} content of samples of ocean water from currents into which meltwater can flow, exclusive of samples from depths greater than 1000 m. The δ for the fresh water contaminant, determined by extrapolation to zero salinity, is —20‰. (See also Curve I, Fig. 1.)

markedly from this Curve and lie closest to Curve II are the two samples from the Mediterranean (Nos. 58 and 59) of salinities 38·7 and 38·8.

A mechanism that will produce this greater change can be readily visualized by comparing the existing evaporation and condensation with that occurring in a several stage distillation column where the amount of liquid in the reservoir flask is large compared to the liquid in the column. In order that several stage fractional distillations be accomplished both evaporation and condensation (i.e., refluxing) must take place in the column. If condensate does not return to the reservoir flask, the resulting product will be of the same composition as the initial vapour that comes off the surface of the liquid in the flask (a single stage distillation). On the other hand, if the reservoir liquid both evaporates and receives back liquid condensed in the column, the composition of this condensate will be deficient in more volatile material relative to the initial vapour that came off the surface of the reservoir liquid and the remaining vapour will be more volatile. Continuous evaporation and condensation provides a mechanism for removing a fraction from the liquid reservoir that is more volatile than would be expected from a single evaporation step, provided that the resulting distillation product is removed from the evaporation-condensation system. If we can consider the formation of ice and its accumulation in the colder regions of the earth as the

mechanism by which the distillation product is removed from the cycle, and if we assume that the distillation product has gone through approximately a three stage distillation, then the existence of snow and ice masses whose O^{18} content, i.e. δ, is approximately $-20‰$ relative to that of the average ocean water as well as the observed depletion of O^{16} from the surface layers of the ocean is explained.

Our data tell very little about the changes in isotopic composition of water

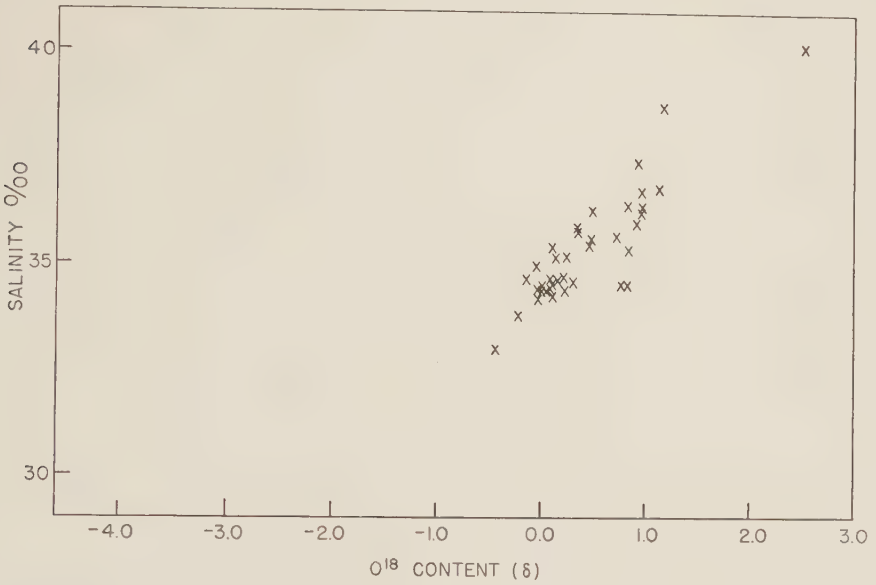

Fig. 3. Relation between salinity and O^{18} content of samples of ocean water from currents that cannot be contaminated directly with meltwater, exclusive of samples from depths greater than 1000 m.

during the intermediate steps between its evaporation from the surface of the ocean and its accumulation as snow in the high latitudes and altitudes. Obviously there are many factors that control the final isotopic composition of snow and ice. Isotopic analysis of water from clouds, from the atmosphere in various places and at various heights and under many different conditions may add information about the processes involved in the transfer of water from one part of the world to another. It is noteworthy, however, that if the O^{18} content of Lake Michigan and Mississippi River waters are typical for fresh waters up to latitudes of approximately 50°, then the water precipitated over the largest part of the earth has an O^{18} content similar to that resulting from the initial evaporation of surface ocean waters. In other words, the fractionation steps which change the O^{18} content of precipitated water from approximately $-7‰$ to approximately $-20‰$ occur in areas close to and possibly in the permanent ice regions. The smaller these areas become and the further north they are pushed by changing world climate, the less water of δ equal to $-20‰$ should be depleted from the oceans. The present vast areas of permanent ice fields keep the surface layers of the present warm oceans enriched in O^{18} by approximately δ equal to $1{\cdot}0‰$. During non-glacial

periods this enrichment should disappear within the present experimental error of measurement.

Data from surface samples of Bermuda marine water illustrate the concept of isotopic fractionation as it is presented here. These samples (Nos. 41–45), which were collected over a period of a few weeks, show a salinity range of 1·4‰ while the O^{18} content (δ) differs by 0·33‰. The change of δ per unit of salinity is thus 0·23‰. This would be expected if evaporation caused depletion of approximately −7‰ water. Local variations of salinities over a short range of time should be accompanied by such changes of O^{18} content. Repeated evaporation and condensation over a long period of time, however, should result in a depletion of H_2O^{16} from the area. This is illustrated by the Bermuda sample (44) which has the lowest salinity, only slightly higher than that of the mean for ocean water, but nevertheless is enriched in O^{18} by 0·8‰ relative to the mean for ocean water.

Data from the Mediterranean Sea are unique in that the difference in δ between the value for this sea and that of the mean for the open ocean relative to the difference in salinities is 0·25‰. Such a relationship would indicate that the "light" water ($\delta = -20$‰) is depleted to a lesser degree from the Mediterranean than from other warm ocean surfaces. Two factors may contribute to this state. They are: (1) the evaporation from the surface which is three times greater than precipitation (Sverdrup *et al.*, 1942), and thus reproduces to some degree the all-evaporation and no-condensation condition where only water with a δ of −7‰ is lost; (2) the greater amount of mixing of the Mediterranean waters so that a large amount of the "light" water per surface area would have to be depleted from the sea before the O^{18} to salinity relationship would approach that present on the relatively thin layer of mixed waters in the Atlantic and Pacific Oceans.

Generally, the conclusion drawn from these data is that large areas of permanent snow and ice increase the amount of variation of the O^{18} content of the oceans by direct mixing of water from the melting ice and by the production of water of higher O^{18} content in the warmer ocean surfaces.

Since the majority of faunal assemblages live or lived in the shallow waters, the postulated effect of glaciers on the O^{18} content of ocean waters is particularly relevant to the problem of determining paleotemperatures by measuring the relative O^{18}/O^{16} ratios in the $CaCO_3$ of marine fossils.

The isotopic temperature scale has been formulated to be

$$T = 16{\cdot}5 - 4{\cdot}3(\delta_1 - A) + 0{\cdot}14(\delta_1 - A)^2$$

where T is the temperature in °C, A equals δ for the water in which the $CaCO_3$ is precipitated and δ_1 refers to the oxygen composition in the $CaCO_3$. Clearly T depends on both A and δ_1 and A is an unknown quantity when paleo-oceans are considered. Consequently, the more homogeneous the O^{18} content of the waters in the oceans of the past, the less uncertain will be the determined T. Fig. 1 shows that with the normal salinity range of 32–38‰, the δ of the oxygen of the $CaCO_3$ in two marine animals living at the same temperature can vary by 2·4‰. In terms of the temperature scale this range would represent an uncertainty in the determined paleotemperature of 11°C. On the other hand, if precipitation of

$CaCO_3$ occurs in the absence of glaciation, that is when the change in δ per unit of salinity is approximately 0·2‰, a 5‰ fluctuation in salinity would be accompanied by a 1·0‰ fluctuation in the O^{18} content of the oceans. This represents a 5°C uncertainty in paleotemperature determinations. Absence of melting glaciers would eliminate a large source of fresh water resulting in greater certainty in measuring paleotemperatures by the isotopic method.

Deep ocean waters

An interesting phenomenon is shown by considering salinities versus O^{18} content of samples of ocean water collected at depths greater than 1000 metres. For a given salinity, the deeper samples are lighter in O^{18} (Fig. 1). For example, sample 22 which is located near the equator at a depth of 7500 metres has a salinity very close to that of the mean for ocean water, 34·8 and a value for δ of −0·47. A possible explanation of this fact is that this sample was collected from one of the deep ocean currents. These currents resulting from sinking polar waters, flow to the equatorial region and thus add what was originally surface water. Such surface water could result from addition of melted snow at first and subsequent freezing out of fresh water from the less saline water of low O^{18} content, the latter process being accompanied by little isotopic fractionation.

Samples of unusual isotopic composition

Included in Table 1 are samples whose isotopic composition is markedly different from that expected of water from the usual natural sources. Sample 90 was collected off the shore of Greenland during the summer, when salinity of surface water is considerably lowered by fresh water from melted ice. From its salinity of 16·2 and O^{18} analysis of $\delta = -11{\cdot}1$‰ it is readily calculated that the δ for melted glacial ice is −21‰. This value confirms the one previously assigned to meltwater.

Samples 48 and 57, located near swamplands in Florida, whose respective salinities are 29·6 and 28·3 and O^{18} analyses 3·5‰ and 4·5‰ could result from mixture of near average ocean water and fresh water analyzing 23·8 and 24·4‰. In this case it would seem that the fresh water which is unusually enriched in O^{18} is a residue of a highly evaporated body of fresh water. We have not been able to verify this conclusion by reference to local conditions.

Sample 102, condensate from a fumarole at Parícutin, is high in O^{18} by 6·75‰ relative to the mean value for ocean water. Lack of the equivalent enrichment in deuterium shows that the enrichment in O^{18} is not due to the method of its collection. Friedman (1953) has shown that the deuterium concentration in this particular sample is nearly the same as that of Lake Michigan water. On the other hand, Silverman (1951) has shown that oxygen isotopic composition is about the same in the silicates of the basalts. The O^{18} enrichment of this sample must then be due to high temperature equilibration with the silicates. Silverman points out that if the oceans were initially composed of juvenile water having the O^{18} content of the basalts, the present day oceans may have gained their present isotopic composition by cold water equilibration with silicates

and carbonates deposited as sedimentary rocks. This results in enrichment of O^{18} in the carbonates and silicates relative to the water in which they are formed.

Summary

The oxygen isotopic analyses of marine and fresh waters, in conjunction with salinity data in the former case, provide information on evaporation and condensation processes in existing water bodies. A large fraction of the fresh water removed from the warm ocean current areas is isotopically similar to the ice and snow found in Greenland and in the mountains in the northwest of North America rather than to the waters in the Great Lakes or typical rain water. The lowering of salinity in the cold Alaskan and Californian currents seems to be primarily due to meltwater from snow and ice. The existence of large bodies of ice and snow seems to play an important part in determining both isotopic composition and salinity of shallow ocean waters. The isotopic composition of fresh water varies over a large range and is dependent upon its history and its source.

Acknowledgments—The authors are indebted to Dr. H. C. Urey for his encouragement, interest and participation in this problem.

Many thanks are due to those mentioned in the text for providing us with samples of water.

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Observations on the geochemistry of indium

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SUMMARY

Spectrographic observations are recorded on the occurrence of indium in sulphide minerals, largely of Australian origin, with a view to determining (a) how traces of indium have been partitioned between primary sulphides; (b) the influence of temperature etc. in partition equilibria; (c) the subsequent behaviour of indium in unmixing processes and secondary mineral formation.

Comparison of minerals from the same sources shows indium to be absent or low in primary iron sulphides, chalcopyrites etc., but preferentially incorporated in blende and, in lesser degree, galena. In minerals of thio-salt type, indium may be highly enriched in enargite and stannite, but virtually absent from tetrahedrite. In any one mineral field, indium is present in higher concentration in blendes or galenas deposited at higher temperatures.

Except for galena, minerals preferentially incorporating indium as sulphides are based on tetrahedral coordination. The selectivity exhibited, and the fate of indium in ex-solution processes, are considered in the light of the structure of indium sulphide and the constitution of quasi-metallic sulphides.

The association of indium with tin in cassiterites from Tasmania and New South Wales is considered. Recorded concentrations give some evidence of geochemical zoning.

In a recent paper D. M. Shaw (1952) has discussed the terrestrial abundance and distribution of indium, with particular reference to igneous rocks, silicates and oxidic minerals. In view of the importance of sulphide minerals as practical sources for the extraction of indium, it appears desirable to put on record some systematic (albeit only semi-quantitative) observations made some years ago on the occurrence of indium in natural sulphides and related minerals.

In the course of a search for practical sources of indium, carried out in Melbourne in 1940–41, it was found that indium was present in appreciable enrichment in various materials—flue dusts, mattes and other by-products—derived from the metallurgical industries of eastern Australia. These included, in particular, products arising from the Broken Hill ore complex and from tin ores from several sources. As a contribution both to the trace geochemistry of sulphide minerals and to the general problem of recovering the rarer elements, it was thought worth-while to examine more closely the sources from which indium is introduced into the sequence of processes involved in the smelting industries.

Indium forms no minerals of its own, but invariably occurs dispersed, as a minor constituent of the minerals of other more abundant elements. As has been apparent since the work of V. M. Goldschmidt, the present distribution of such minor constituents should be capable of interpretation in terms of physico-chemical principles, involving (a) atomic similarity between elements, in the sense of similarity in ionic or covalent radii; (b) the physico-chemical variables (temperatures, concentrations, etc.) associated with the segregation of crystalline phases from melts or high temperature solutions; and (c) the operation of specific chemical properties, which have modified distribution during secondary chemical changes undergone by the original mineral species. The first factor has led to the association of elements from the same "horizontal" period of the Periodic

Classification—e.g. the association of indium with silver, cadmium, tin and antimony (in sulphide minerals), clearly established by Brewer and Baker (1936) and the analogous association of germanium with its neighbours, in enargite and germanite. (Papish *et al.*, 1927; W. S. Thomas *et al.*, 1927).

Goldschmidt, Fersman and others have given full discussions of the second factor, as applied to the distribution of trace elements in silicates and oxides, and Shaw's paper (1952) deals with the specific case of indium. It is, however, hardly possible to extend the same treatment to sulphide minerals, because of lack of experimental material and because the heavy metal sulphides cannot be regarded as pure ionic solids.

It is considered that the primary sulphide minerals have been formed in a moderately well-defined sequence from an originally homogeneous high temperature liquid (Niggli, 1937). As deposition proceeded, and the temperature fell, the relative concentrations of major and minor constituents in the residual liquid changed also. Furthermore, minerals of different structure, undergoing deposition simultaneously from the same liquid, are unlikely to have incorporated with equal ease the atoms of a trace constituent such as indium. The behaviour of trace elements in sulphides cannot be predicted in the same way as is possible for ionic structures, and the factors determining their distribution, both during the initial formation of primary minerals and in secondary processes of differentiation, must be evaluated empirically in our present state of knowledge.

As a contribution to this theme, two problems were posed: (i) how have traces of indium been partitioned between the primary sulphide minerals, as indicated by the indium content of minerals of cognate origin? (ii) how does the concentration of indium in any one mineral species (e.g. in zinc blende) vary with the conditions (e.g. temperature) of mineral formation, as recognised geologically and exemplified both by specimens from different mineral deposits and by specimens from different locations in one major region of mineralisation, or even within a single ore body?

Russian work on the geochemistry of trace elements (and of indium in particular) has followed much the same lines as that described here (for the fundamental geochemistry of indium see, especially refs. Prokopenko, 1941 and Borovik *et al.* 1939); for regional surveys Prokopenko, 1941, Borovik *et al.* 1938, Kalinin, 1941 and Lamanov, *et al.* 1938. This Russian work, which came to the author's notice after the bulk of the work had been done, represents a valuable and systematic application of geochemistry to the problem of extracting the rarer, but economically useful, elements.

Experimental

Samples examined. Specimens of the principal sulphide minerals, associated minerals, and minerals derived from them by secondary chemical changes, were obtained from a wide range of sources. Most of the specimens were from eastern Australia and Tasmania, being obtained from known locations in certain of the principal ore deposits. It was, in particular, possible to obtain a range of samples from the Broken Hill field, and from the bornite-chalcopyrite ores of Mt. Lyell. All specimens were of high quality, and the mineralogical purity of many of them was known from mineragraphic investigations carried out by Dr. A. B. Edwards, of the Commonwealth Scientific and Industrial Research

Organisation. About 120 sulphides and related specimens were examined; the work could profitably be extended. In addition to the sulphide ores, observations are recorded for 65 samples of cassiterites from Tasmania, the New England district (N.S.W.) and other localities. For most of these analyses, the author is indebted to Mr. A. W. Thurstan, chief chemist of *O. T. Lempriere Pty. Ltd.*, and to *Messrs. Lempriere's* who made the samples and their own results available.

Table 1. *Sphalerites*

		In	Cd	Sn	Sb	Ge
MS3	Broken Hill, Location unknown	+	s	m	wm	—
M1	Broken Hill, Sulphide Corporation	—	ms—	w	vw	—
ZC3	Broken Hill, North Mine 1850′ stopes	+(+)	ms	vvw	—	—
ZC1	Broken Hill, North Mine 1850′ stopes	++++	ms(=In)	w	—	—
E1	Broken Hill, Zinc Corporation, 4 S.W. stope, No. 12 level	—	s	vw	vw	—
ZC4	Broken Hill, Zinc Corporation	+++	ms(In)	w	vvw	—
ZC2	Broken Hill, South Mine	++	ms	w	—	—
ZC7	Broken Hill, South Mine	v.s.	w	ms	ms?	—
ZC41	Broken Hill, South Mine, 1070 level, 6–7 West Pillar	?	ms	mw	—	—
ZC41A	Broken Hill, South Mine, 1070 level, No. 7 W. stope	?	ms	vvw	vvw	—
ZC14B	Broken Hill, South Mine, 1070 level, No. 10 W. stope	—	ms	vvw	vvw	—
E30	Lake George Mine, Captain's Flat, N.S.W.	+	ms	ms	—	—
E23	West Lyell, Tasmania	—	ms	vw	vw	—
E25	Lyell Tharsis, Tasmania	—	w	vw	—	—
S5	Swansea Mine, Zeehan, Tasmania	—	ms	—	w	—
E38	Swansea Mine, Zeehan, Tasmania	—?	ms	m	—	—
E7	Rosebery, Tasmania, Copper lode, No. 8 level	—	m	vw	vvw	—
MS2	Aurora, U.S.A.	—	m	—	—	+++
S4	Joplin, U.S.A.	—	s+	s	w	++
S3	Oklahoma, U.S.A.	—	ms	—	w	+
S2	Franklin Furnace, N.J.	—	s	s	w	—
S1	From New Jersey Zinc Co.	—	vs	ms	wm	—
S6	St. Christophe, Breitenbrunn	+	ms	m	w	—
E27	St. Christophe, Breitenbrunn	—	ms?	m?	—	—

Key to Table

—	indium not detected: limit of detection	0·0005%
+	indium definitely detected :	0·0005 — 0·002%
++		0·002 — 0·01%
+++	relatively rich in indium :	> 0·01%

Spectroscopic observations. Most of the observations were made using a Hilger medium spectrograph, with quartz optics. The samples were volatilised as completely as possible, without carrier, from the positive crater of a d.c. arc (10 amp.).

The dispersion of the available instrument virtually restricted the detection of indium to the sensitive lines at 3256·090 Å and 3039·356 Å (wavelengths from M.I.T. tables). The former line may be subject to interference by the Mn line 3256·137 (intensity 75) and the Fe line 3255·890 (intensity 20); such interference is indicated by the presence, at comparable strength, of the Mn lines at 3260·231 (75), 3258·413 (75), 3254·039 (50), 3252·948 (75) and 3251·135 (50), or of the Fe lines at 3259·994 (150), 3253·949 (20) and 3252·926 (80) (wavelengths and intensities from M.I.T. tables). The line at 3039·356Å is subject to interference from Fe 3039·316 (20). These close lines greatly reduced the sensitivity of detection of indium in the iron sulphide minerals. Through the courtesy of *Messrs. General Motors-Holdens Ltd.*, however, a number of specimens were examined under the higher dispersion of a Hilger Littrow spectrograph, with which it was also possible to utilise the lines In 4511·32 and In 4101·77, which are free from interference.

Table 2. Galenas

		In	Cd	Sn	Sb	Ge
ZC11	Broken Hill, North Mine (N.S.W.)	++	w	ms—	ms –	–
ZC27	Broken Hill, North Mine Northern Orebody (Calcite) 2300′ level. Lower temp.	—	w		w	—
ZC9	Broken Hill, North Mine Southern Orebody (Rhodonite) 2300′ level. Higher temp.	+ (just)	w		ms	—
E2	Broken Hill, Zinc Corporation Mine	—?	w		ms	—
ZC10	Broken Hill, Zinc Corporation Mine	+(+)	(=In)		m	—
ZC43	Broken Hill, South Mine 1070′ level No. 7 W. stope	—	w		wm	—
ZC42	Broken Hill, South Mine 1480′ level No. 7 E. stope	—	w		ms	—
ZC8	Broken Hill, Junction Mine	+(v.w)	—		—	—
MS1	Broken Hill, Silverton, Gypsy Girl Mine	—	—		w	—
E31	Lake George Mine, Captain's Flat, N.S.W.	+++	—		w	—
E34	Tri-state district, U.S.A.	—	—		w	—
E49	Northampton, W.A.	—				
E14	Mt. Lyell, Open Cut (Tasmania)	+(+)	—		w	—
E13	West Lyell (Tasmania)	—	s		vw	—
E28	North Lyell (Tasmania)	—	—		vvw	—
E12	Lyell Comstock (Tasmania)	—	vvw		mw	—
E11	Tasman Lyell (Tasmania)	—	mw		w	+
E6	Rosebery, Tasmania: Copper Lode, No. 8 level	—	—		ms	—
E41	Renison Bell, Tasmania	+	—		—	—

Table 3. Thio-salt minerals

		In	Cd	Sn	Sb	Ge
S22	Tetrahedrite: Broken Hill, Zinc Corporation Mine	—				—
E32	Tetrahedrite: Lake George Mine, Captain's Flat, N.S.W.	—				—
E10	Tetrahedrite: Rosebery, Tasmania	—(?)	+	—		—
E5	Tetrahedrite: Rosebery, Tasmania, Hercules Mine	+ (limit)	—	—		—
E24	Enargite: Mt. Lyell—open cut	++	w	—		—
E37	Enargite: Butte, Montana	—	—	—	ms	+
G1	Stannite: Conrad Mine, N.S.W.	+++				+
E50	Stannite, Oonah Mine, Zeehan, Tasmania	+++				—
M6	Sulvanite, Edelweiss Mine, nr. Burra Burra, S.A.	—				
S21	Bournonite: Broken Hill	—	vw	vw		—
E36	Boulangerite: Ob Lahr, Rhine	—	—			

Results in Tables 1–3. 6–9 are expressed on a qualitative basis. From cognate experiments on industrial by-products, using a logarithmic sector, the symbols correspond roughly with the following indium concentrations.

Key to Tables

—	indium not detected: limit of detection	0·0005%
+	indium definitely detected:	0·0005 — 0·002%
++		0·002 — 0·01%
+++	relatively rich in indium:	>0·01%

In a few cases, spectrographic determination was supplemented by chemical enrichment experiments; these are dealt with in the discussion section.

Results

Results of the spectroscopic analyses of sulphide minerals are summarised in Table 1 (zinc blendes). Table 2 (galenas) and Table 3 (tetrahedrites, enargites and other complex sulphides). In addition to the series set out in full in Tables 1–3, the following iron sulphide mineral specimens were examined (Table 4), with completely negative spectrographic results.

Table 4

Pyrites and marcasites

ZC31	Broken Hill, North Mine 1850′ stopes
ZC26	Broken Hill, Zinc Corporation Mine
E17	Mount Lyell, Tasmania
E18	Prince Lyell Mine, Mt. Lyell, Tasmania
E9	Rosebery, Tasmania
E45	Moonta, S.A.
—	Cooper's Creek, Walhalla, Victoria
S9	Leadville, Colorado
S10	Marcasite, Ottawa City, Okalahoma
MS4	Marcasite, Aurora

Pyrrhotites

ZC25	Broken Hill, North Mine, Southern Orebody 2000′ level
S8	Broken Hill, Zinc Corporation Mine
ZC22	Broken Hill, Zinc Corporation Mine
E4	Broken Hill, Zinc Corporation Mine, 1962′ level 4 N.E. section
ZC24	Broken Hill, South Mine
ZC36	Broken Hill, British Mine
—	Cooper's Creek, Walhalla, Victoria
—	With pentlandite, Cooper's Creek

Chalcopyrites

E19	Mt. Lyell, Tasmania
E22	North Lyell, Tasmania
M4	From epidote dyke, Cooper's Creek, Walhalla, Vic.
E46	Moonta, S.A.
E44	Moonta, S.A. (with secondary covellite)
M5	Bethanga, Victoria
S11	Bisbee, Arizona

Bornites

E43	Moonta, S.A.
E21	Mount Lyell, Tasmania
E29	North Lyell, Tasmania
E20	Comstock Lyell, Tasmania
M35	Erubescite: Location unknown

Arsenides

ZC29	Löllingite, Broken Hill North Mine 1850′ stopes
E3	Löllingite, Broken Hill, Zinc Corporation Mine No. 8 level 6 N.W. stope
ZC28	Löllingite, Broken Hill, Zinc Corporation Mine
M3	Arsenopyrite, Ottery Mine, Torrington, N.S.W.
S13	Arsenopyrite, Freiberg, Saxony
ZC30	Cobaltite, Broken Hill Consols Mine, N.S.W.
E40	Cobaltite, Mt. Cobalt, Queensland
E30	Smaltite, Cobalt, Ontario

The sources of these negative specimens are recorded, for comparison with blendes, galenas etc., from the same locations.

The minerals from Cooper's Creek, Walhalla, are representative of an unusual, high temperature hydrothermal deposit, containing pyrrhotite and pentlandite (both relatively rich in palladium), platiniferous pyrite and sperrylite. The whole is geochemically comparable with the nickel ore of Subdury, Ont. (Edwards, 1947).

As already stated, indium was not detected by direct spectrographic observation in any of the iron minerals, but the lower limit of detection was considerably above that obtaining in the investigations of the non-ferrous minerals, and a low indium content might have escaped detection. Other workers (cf. Brewer and Baker, 1936) have reported the presence of indium in chalcopyrites, and the crystal-chemical considerations advanced below suggest that where chalcopyrite is associated with indiferous zinc blend, some indium should be found in the chalcopyrite also. Certain of the chalcopyrites, pyrrhotites and pyrites were accordingly treated to effect an enrichment and separation of indium from iron.

Two methods of enrichment were examined. In the first, which was suitable for chalcopyrite or other minerals rich in copper, the mineral was dissolved in hydrochloric acid and bromine. Copper was removed from the solution either by electrolysis at a carefully controlled cathode potential, or by shaking the solution with zinc amalgam. A platinum wire cathode was then introduced, and the potential across the cell raised to 2.5 volts. Blank experiments showed that 1γ of In could be recovered from 50 ml of solution by this means. The cathode deposit was dissolved, and any indium was precipitated as hydroxide on aluminium hydroxide as carrier. Indium was clearly detected in chalcopyrite E52 (probable concn. 0·0001–0·001%), but could not be detected in chalcopyrite closely intergrown with galena ZC2.

A second enrichment method was applicable to zinc blendes etc. The mineral was dissolved in hydrochloric acid and iron, if present in large amount, was reduced to the ferrous state. The solution was then shaken with successive portions of freshly precipitated barium carbonate, to act as collector.

Binary sulphides

An examination of the results summarised in the foregoing tables shows that, where a genetically related deposit of sulphide minerals, as a whole, contains significant amounts of indium, the crystal lattice of zinc blende is one preferential host for the indium present; also that the galena associated with indiferous blende incorporates indium. The data also exemplify the "horizontal" association of indium with silver, cadmium, tin and antimony, although there is no clear correlation between the amounts of the minor elements. The results emphasise the very variable content of minor constituents in different specimens of any one mineral, even when taken from different locations in the same region of mineralisation.

In agreement with the statements of Russian geochemists, there is a general correlation between the indium content of zinc blendes and their colour (or iron content). The latter, in turn, is an index of the temperature of deposition of the

sulphide. Broken Hill zinc blende is typical marmatite ("black jack") whereas the American blendes in Table 1 were all light coloured. The deposits referred to in Table 1 probably fall into the temperature sequence:

High temperature . . .	Broken Hill
Moderately high temperature .	Captain's Flat; Swansea; Rosebery
Moderate temperature . .	Mt. Lyell
Low temperature . . .	American fields cited

(Dr. A. B. Edwards'—private communication)

Amongst the specimens from Broken Hill, there is evidence for a greater concentration of indium in the lower ore body (associated with rhodonite and garnet) than in the upper ore body (associated with calcite). There is thus a correlation of indium content and temperature of deposition within the one field.

The minerals from these sources may originate from materials of substantially different total composition, but the evidence suggests a distribution equilibrium between indium incorporated in the growing zinc blende phase and that in the residual liquid at each stage. If so, it is probable not merely that the residual liquid became impoverished in indium, through preferential incorporation in the first fractions of solid, but that the distribution coefficient altered, in favour of the solution phase, as the temperature fell. Thus an enrichment experiment indicated the presence of indium at a concentration of about 0·0000x% in the (nearly colourless) cleiophane S1, whilst (as indicated below) other minerals following zinc blende in the sequence of deposition became the preferred collectors of the residual traces of indium.

An apparent exception to the correlation between colour and indium concentration is presented by the exceptionally rich, honey coloured blende ZC7. With about 0·08% indium, this represents one of the richest specimens recorded. This was identified, however, as a secondary mineral (by its banded or "colloform" structure (Edwards, 1947)), and there is no doubt that it originated from a fractional precipitation as an acid solution, derived from the leaching of the primary minerals, underwent progressive neutralisation and re-deposition of sulphides.

There is not a clear relation between the indium contents of galenas and associated zinc blendes; the latter may be either richer (as at Broken Hill) or poorer (e.g. at Captain's Flat) in indium. Galena, like blende, shows a distinct correlation between indium content and temperature of deposition, both as between different deposits and within the same mineral field. Locations of minerals in the Mount Lyell are quoted in Table 2 in the order corresponding to the presumed decreasing temperature of mineralization. Indium was detected only in galena E14 (and also in enargite E24) from the high temperature end of the field, and germanium only at the low temperature end (E11). Whilst the latter observation may be fortuitous, it is noteworthy that germanium was detected only in the low temperature zinc blendes (S2, S3, S4) and in secondary copper sulphides related to them (S18, S19).

Galena E41 is an unusual occurrence of this mineral, associated with a cassiterite which contains about 0·005% indium. It is stated that this galena

probably originated in the last stages of pneumatolytic differentiation of magmatic material (Stillwell *et al.*). It appears to have shared with cassiterite the function of collector for the trace of indium contained in the residual liquid.

Thio-salt minerals

A noteworthy feature of Table IV is the virtual absence of indium from the tetrahedrites examined. This is particularly significant in the case of E32, which is associated with a blende (E30) and galena (E31) both of which are relatively rich in indium. Enargite is a fairly high-temperature mineral, considered to have been deposited before or concurrently with zinc blende; reference has already been made to its role as a collector of trace elements. Sample E24, from the higher temperature end of the Mt. Lyell field, although a very minor mineral, is very much richer in indium than any of the major primary sulphides with which it is associated. It is clear that the distribution equilibria were such as to favour a selective incorporation of indium in the enargite structure. It is, therefore, of interest to observe that the Montana enargite E37 contains no detectable indium, although it contains germanium; this could point to a significant difference of composition between the original magmatic materials of the two mineral provinces concerned.

The other thio-salt minerals were mostly deposited after, and at a lower temperature than, galena. Brewer and Baker (1936) showed that complex tin sulphides may contain relatively high concentrations of indium. This appears to be true of stannite (contemporary with galena). Thus E50 was one of the richest minerals found although the principal sulphide minerals from West Tasmania generally have a low indium content. This may be seen by comparison with minerals from Mt. Lyell and from the Rosebery field (e.g. E6, E7). However, the presence of indium in flue dust obtained in roasting the Rosebery ore probably implies the presence of indium in the major minerals, below the limit of direct detectability.

As has already been stated, the incorporation of trace elements in sulphides and related minerals will be governed by somewhat different considerations from their incorporation in ionic crystals. Sufficient similarity in atomic size between host and substituent is necessary to avoid excessive distortion; the sizes concerned will, however, be essentially the covalent radii of the atoms for a certain co-ordination number. Since, however, the binding forces are predominantly covalent or metallic (i.e. resonating covalences, in the sense of Pauling's description of the metallic bond), the most important factor is the availability of bond orbitals (tetrahedral or octahedral hybrid orbitals) suited to the stereochemical arrangement imposed by the host crystal. The number and bond-order of the bonds formed, and the energies involved in changes of electron configuration, will determine the energetics of substitution in the crystal lattice of the host. In this substitution, however, there is not the same restriction of electrostatic balancing, as applies to ionic crystals. The sulphide minerals are either semiconductors or quasi-metallic, and are often phases of variable composition, and the inclusion of atoms of lower or higher formal valency than the atoms of the host is rendered possible by entry of additional electrons into the conduction band of the crystal,

or by creation of positive holes. The energetics of substitution may, for this very reason, be affected in a rather subtle manner by the electron concentrations (i.e. the oxidation reduction potential) of the melt from which the minerals are deposited.

In considering how these principles apply to the observed facts, it is to be noticed, in the first place, that the minerals observed to contain significant amounts of indium conform to a common structural type. Zinc sulphide (both as blende and as wurtzite), chalcopyrite, tetrahedrite, stannite and enargite are all based on cubical close packing of sulphur atoms, with the metal atoms occupying positions of tetrahedral coordination. The four minerals last mentioned, and also bornite, are explicitly recognised by Buerger (1947,1949) as "derivative" structures of the zinc sulphides; thus chalcopyrite is related to blende by the substitution of half the zinc atoms by copper atoms, and half by iron, in an ordered manner and with little dimensional change. There is evidence that, at high temperatures, the metal atom sites in these structures become equivalent, through an order-disorder transition, so that they acquire a pseudo-zinc blende (or wurtzite) structure, and display a considerable measure of miscibility with one another. Thus bornite (Sugaki, 1951) and tetrahedrite (Edwards, 1946) are completely miscible with chalcopyrite above 450–500°, and zinc blende is also

Table 5

	Substance	*Interatomic distance* Å		*Coordination*	*Ref.*
ZnS	Zinc blende Wurtzite	Zn–S	2·35 (2·71)	Tetrahedral (hypothetical octahedral)	
$CuFeS_2$	Chalcopyrite	Fe–S Cu–S	2·20 2·32	Tetrahedral	
Cu_3SbS_3	Tetrahedrite	Cu–S Sb–S	2·1–2·23 2·43	Tetrahedral	Machatschki, 1928
Cu_2FeSnS_4	Stannite	Cu–S Fe–S Sn–S	2·31 2·36 2·43	Tetrahedral Tetrahedral	Brockway, 1934
Cu_3AsS_4	Enargite	Cu–S As–S	2·31 2·24	Tetrahedral	Pauling *et al.*, 1934
Cu_3VS_4	Sulvanite	Cu–S V –S	2·28 2·19		
PbS	Galena	Pb–S	2·96 (2·57)	Octahedral (hypothetical tetrahedral)	
α–In_2S_3	Blende-like (metastable)	In–S	2·32 2·68	Tetrahedral octahedral	Hahn *et al.*, 1949
β–In_2S_3	Pseudo spinel	In–S	2·53 2·58	Tetrahedral octahedral	Hahn *et al.*, 1949
$CuInS_2$	Chalcopyrite-like	M–S average 2·39			Hahn *et al.*, 1949
$AgInS_2$	Chalcopyrite-like	M–S average 2·49			

stated to be miscible with chalcopyrite at higher temperatures. Where, as at Broken Hill (ZC2A) and Captain's Flat (E52), chalcopyrite is a very minor constituent, closely intergrown with zinc blende, it has probably been formed by the unmixing and segregation of such a solid solution. It is therefore of interest that no indium was detected after an enrichment experiment on ZC2A, and only a low concentration (detected as a result of an enrichment process) in E52, although in both cases the associated blendes had 0·002–0·01% In. The equilibrium distribution was this very uneven, and it is necessary to examine the structural factors which may exercise a specific effect.

Table 5 gives a survey of the metal-sulphur distances in the native sulphides concerned, and in synthetic indium sulphide of known structure. The structure and In-S distances in InS and In_2S are, unfortunately, not known, but β–In_2S_3 has a pseudo-spinel structure (Hahn *et al.*, 1949) involving both 4– and 6– coordinated indium. It has also been found that indium sulphide combines with other sulphides to form chalcopyrite-type (Hahn *et al.*, 1952) or thio-spinel type (Hahn *et al.*, 1950) structures, indicating that indium has a strong tendency to form tetrahedral bonds in sulphide structures, but can also occupy octahedral positions. In terms of the formation of covalent-bonded structures (with fractional order bonds), this is understandable. The ground-state configuration of the indium atom is KLMN $5s^2 5p$, and the formation of tetrahedral covalent bonds, using $[5s5p^3]$ orbitals, is likely to be preferred energetically, as compared with octahedral bonds, requiring the use of 6*d* levels also.

It is evident from Table 5 (a) that (except for galena, which is considered below), the sulphides serving as collectors for indium are all based on tetrahedral coordination; (b) that the In-S tetrahedral bond length in stable structures is considerably greater than the Zn–S, Cu–S or Fe–S bond lengths*, being most closely approached by the Sn–S bond length in stannite, which is one of the most efficient collectors of indium; and (c) that the minerals rejecting indium most completely are those with the smallest mean M–S bond length. There is thus some evidence that, insofar as the dimensional factor is important for the immiscibility of zinc blende with its derivative structures at low temperatures, it also causes the distribution coefficient of indium to favour the zinc blende phase. The effect of lattice strain may be intensified by a more specific chemical factor: indium can apparently replace iron, but not copper, in chalcopyrite-type structures (cf. the different behaviour of indium sulphide with copper and iron sulphides), thereby making the incorporation of indium still less favourable. Incorporation of an indium atom on a proper lattice site in zinc blende or its derivative structures thus involves a strongly positive free energy change; as such, the solid solubility of indium sulphide in zinc blende (or related structures) will be favoured by an increase in temperature. Higher temperatures also provide a means of incorporating foreign atoms, through the creation of lattice defects in thermal equilibrium—i.e. vacant sites and (as is frequently assumed for structures of ZnS type) interstitial atoms. Although the sulphides are semiconductors, solute atoms which contribute more or less than the average number of electrons to the valence band

* If the indium has to be incorporated in a state of effectively lower valency (e.g. as quasi-univalent, forming bonds from its ground state), the covalent radius would be still greater.

of the crystal (2 per metal atom, in the case of ZnS-like structures) may involve the simultaneous creation of lattice defects; Braekken (1934) has given some not very convincing reasons for supposing that zinc blendes containing iron also have a high concentration of vacant sites. If this is so, it is possible that a foreign atom may be associated either with a vacancy, or with an atom of smaller covalent radius, thereby minimising the distortion.

It is, alternatively, not impossible that at high temperatures, where there is a significant concentration of interstitial atoms, foreign atoms of appropriate size might be accommodated in interstitial positions instead of on regular lattice points. This possibility is of particular interest in relation to galena, since the Pb–S distance is so much greater than the normal In–S distance that conditions should be extremely unfavourable for substitutional solid solution. The M–S distance for an atom in a (tetrahedral) interstitial position in the galena lattice would, however, be quite appropriate for indium. It may not be irrelevant that, of the minerals concerned, galena possibly has the greatest variability in stoichiometric composition. If this hypothesis is wrong, it would seem necessary to invoke a simultaneous substitution of In + Te (or other very large metalloid) in place of Pb + S. Reference has been made to the "horizontal" association of trace elements. There is no obvious correlation between the amounts of the elements from Ag to Sb (and possible Te) in blendes or galenas; the fact that all tend to be present together need signify no more than that conditions which favour incorporation of one apply more or less equally to all, since the covalent radius changes relatively slowly in traversing such a series of consecutive elements. No simple generalisation can be based on the facts, however; the central problem of this work needs a greater range of observational material, coupled with laboratory experiments.

Secondary minerals

Data for secondary copper minerals and for oxidised lead and zinc minerals are presented in Tables 6 and 7 respectively.

Chalcocite is usually a secondary mineral, replacing bornite or pyrite. With the possible exception of E26 (which may be a primary mineral) the chalcocites listed in Table 6 are considered to be secondary. It would appear that chalcocite can act as a collector of traces of indium arising either from the mineralising solutions or, by residual enrichment, from the copper-iron sulphides replaced. High temperature chalcocite is one of the structures with random arrangement of cations; the metal-sulphur distance from an atom in a tetrahedral position (2·41 Å) is within the range apparently favouring incorporation of indium.

In oxidised minerals, the fate of trace constituents depends on their behaviour during the processes of leaching, neutralisation and deposition of insoluble oxyacid salts. The oxide of indium is a weak base; the hydrated oxide is very insoluble, but the sulphate is soluble. In the minerals of the oxidised zone of Broken Hill, we find indium to be regularly present in cerussite, recalling the use made of the freshly precipitated carbonates of bivalent metals as collectors of indium etc., in laboratory enrichment processes. Pyromorphite can also act as a carrier in the same way, whereas indium was not detected in the sulphate minerals.

Table 6. Copper Minerals

		In	Cd	Sn	Sb	Ge
ZC32	Cuprite: Broken Hill Proprietary Mine	—				—
ZC33	Native Copper: Broken Hill Proprietary Mine	+				—
M9	Chalcocite: Hampden, Queensland	+ vw		+		—
E42	Chalcocite: S.A., exact location unknown	+ vw				—
E33	Chalcocite: Mt. Oxide, Queensland	+ vw				—
E26	Chalcocite: North Lyell, Tasmania	+?				—
E51	Covellite: Moonta, S.A., Bennett's shaft, 60′ level	Possible limit of detection?				
S17	Chalcocite: Montana	++				—
S18	Chalcocite: Bisbee, Arizona	+				++
S19	Covellite: Butte, Montana	—				++

Table 7. Oxidised Lead and Zinc Minerals

		In	Cd	Sn	Sb	Ge
ZC5	Gahnite: Broken Hill	+	—	w	—	—
ZC6	Smithsonite: Broken Hill	—?	m	—	vvw	—
ZC15	Cerussite: Broken Hill, South Mine	+	—		vvw	—
ZC14	Cerussite: Broken Hill, Block 14	+	—		—	—
ZC23	Cerussite: Broken Hill, Proprietary Mine	+	?		?	—
ZC12	Anglesite: Broken Hill, Proprietary Mine	—	—			—
ZC21	Linarite: Broken Hill, British Mine	—				—
ZC16	Pyromorphite: Broken Hill, Proprietary Mine	+	+		+	—
ZC17	Pyromorphite (yellow var.): Broken Hill, Block 14	—	—			—
ZC17A	Pyromorphite (yellow var.): Broken Hill, Block 14	—				—
ZC19	Stolzite: Broken Hill, South Mine	—				—
ZC20	Stolzite: Broken Hill, Proprietary Mine	—				—

Cassiterites

Shaw (1952) has questioned the justification for the statement made by various authors, that indium is systematically associated with tin in cassiterites. Tables 8 and 9 present evidence bearing on this point. Table 8 is a collection of analyses kindly furnished by Mr. A. W. Thurstan, which provides some statistical evidence for the variation of indium content between samples from different sources, and for the variation in composition of samples from one source. These analyses were

Table 8. Cassiterites

	< 0·001	> 0·001 < 0·005	> 0·005%
Mt. Bischoff, Tasmania	0	1	4
Renison, Bell, Tasmania, West Coast	0	2	2
Tasmania, East Coast	0	2	0
West Wyalong, N.S.W.	2	0	0
Bendemeer, N.S.W.	1	0	0
Gibsonvale, N.S.W.	1	0	0
Mt. Tallebong, Condobolen, N.S.W.	2	1	0
Tingha, N.S.W.	7	3	0
Emmaville, N.S.W.	0	1	1
Watson's Creek, N.S.W.	0	1	0
Stannifer, N.S.W.	0	1	0
Deepwater, N.S.W.	0	0	1
Herberton District, Queenland	2	3	3
Stanthorpe, Queensland	1	3	0
Charters Towers	1	0	0

Table 9. Cassiterites

		In	Ge
M10	Mitta Valley, Victoria, from pegmatite dyke	—	—
L5	Mt. Bischoff, Tasmania	++	—
L4	Renison Association Mine, Renison Bell, Tasmania	+	—
L6	Anchor Mine, Blue Tier, Tasmania	++	—
L7	Vegetable Creek, N.S.W.	?	—
L3	Aberfoyle Mine, Tasmania	+	—
L2	Ardlethan, N.S.W.	++	?
L1	Ewen, N.S.W.	+	—
L13	Gibsonvale, N.S.W. Stream tin ore	+	—
L14	Torrington, N.S.W. New Butler Mines: Mill tin ore	+	—
M11	Torrington, N.S.W. New England Mine: Mill tin ore	+	—
L15	Tingha, N.S.W. Tingha South Mine: Stream tin	+(limit)	—
L12	West Wyalong, N.S.W. Kantara Synd. Stream tin ore	—	—
L11	Mt. Tallebong, Condobolen, N.S.W. R. Gentle's	++	—
L10	Emmaville, N.S.W. Gt. Britain Mines: Stream tin ore	++	—
L9	Bendemeer, N.S.W. Cleghorn's: Stream tin ore	+	—
L8	Glen Innes, N.S.W. Stream tin ore	+	—
M12	Nundle, N.S.W.	+	—
L16	Stanthorpe, Queensland. Kyoomba Synd. Stream tin ore	++	—

carried out on metallic tin reduced from the ore. They are supplemented by the data of Table 9, obtained by direct spectrographic examination of the cassiterites. The latter analyses were less sensitive, because of the interfering spectra of the other minor constituents. With the exception of the specimen M10, which (in agreement with Shaw's views) suggests that cassiterite did not act as a very

efficient collector for traces of indium at the stage of pegmatite formation. all the specimens came from one or other of two tin fields: in Tasmania and the New England district of N.S.W. respectively. They consistently contain very appreciable amounts of indium. and a comparison between the average indium content and the geographical distribution of the samples suggests a real geochemical zoning. The data are insufficient, however, for a positive assertion on this point.

Geochemical history of indium

It is permissible to use the results of this survey to amplify our picture of the geochemical cycle of indium.

(a) In accordance with its chalcophile character, the distribution coefficient of indium between liquid sulphide and liquid silicate phases has led to an enrichment of indium in products derived from the sulphide phase of magmatic material. The subsequent course taken by indium in the oxide-silicate phase has been considered by Shaw. It need only be added that the association of indium with tin in cassiterite has been confirmed, and that where (through a further process of phase separation or by secondary processes) there was a fresh deposition of appropriate sulphides, these acted as collectors of indium.

(b) In the subsequent differentiation of the sulphide phase, the distribution coefficient of indium did not favour its incorporation in the first sulphides pyrrhotite. pyrite and arsenopyrite; it will therefore have accumulated in the residual liquid until that stage of the crystallisation process associated with the formation of structures based on 4 : 4 coordination—i.e. enargite, zinc blende and (possibly) chalcopyrite. Enargite and high temperature zinc blende were favoured hosts for indium, but by the time the temperature had fallen so far that zinc blende took up little or no iron, either the residual liquid had been too far impoverished in indium, or the partition coefficient had changed in favour of the liquid phase or of other contemporary minerals. In particular, where stannite or other low-temperature complex thio-salt minerals were formed late in the crystallisation process, these probably acted as scavengers for the remaining indium. Galena acted as a host for indium concurrently with, but probably less efficiently than, zinc blende.

(c) It is not possible to state whether the incorporation of indium in other sulphides is condition by the stoichiometric variability of these substances at high temperatures, or whether inclusion of indium is necessarily coupled with inclusion of other trace elements of higher or lower valency, as is the case in purely ionic crystals.

(d) The results, taken in conjunction with those reported by Shaw and others, lend some support to the ideas of "indium provinces." Indium is characteristic of the Australian minerals examined, whereas germanium (cf American minerals) is not.

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Potassium in ultramafic rocks*

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ABSTRACT

Quantitative spectrochemical determinations of potassium in 50 specimens of ultramafic rock confirm the preliminary observation (Ahrens, Pinson and Kearns, 1952) that the abundance of potassium in this rock type is much lower than has usually been assumed. Observations have been made mainly on dunite and serpentine and in these rocks the potassium concentration averages at about 0·001%. Although it is highly unlikely that the whole of the mantle could have a chemical composition equivalent to pure dunite, a significant proportion may have. In such material the heat contribution by K^{40} at a concentration of 0·001% total K, is $0{\cdot}00025 \times 10^{-6}$ cal/g/yr: this is probably a small proportion (perhaps ~1/100) of that which appears to be generated ($0{\cdot}02 \times 10^{-6}$ cal/g/yr) by the U + Th series.

Introduction

Potassium is of extraordinary geological interest and importance. Not only is it (i) a major constituent of several common minerals, (ii) unusually responsive to processes of fractional crystallization and hence of much petrological and geochemical significance, but (iii) one of its isotopes, K^{40}, is naturally radioactive and exhibits the feature of dual decay, forming Ca^{40} by β decay and A^{40} by electron capture decay. The consequences of this decay are themselves of much geological and geophysical importance: (a) heat production by K^{40} is significant in rocks and may have been a dominant source of earth heat in the earliest periods of earth history. (b) electron capture in K^{40} is probably the main source of atmospheric argon, and (c) K^{40} activity may eventually be satisfactorily utilized for determining geological age—either by an argon method and/or by a calcium method.

The purpose of this paper is to provide some additional geochemical information on the abundance of potassium. Whereas much is known about the abundance of potassium in some of the commonest igneous rocks exposed at the earth's surface, less is known about its abundance in ultramafic rocks. These rocks are of considerable importance because the composition of some of them may closely resemble some of the material which comprises significant proportions of the earth's mantle. Not only are fewer analyses of these rocks available but observations by Ahrens, Pinson and Kearns (1952) indicate that some published determinations may be in error by a whole order of magnitude.

In our investigation, potassium has been determined in 50 specimens of ultramafic rock. Particular attention has been given those varieties which are quantitatively the most abundant, namely, dunite and serpentine.

Analytical Procedure

The Lawrence-Smith fusion procedure has commonly been used to determine sodium and potassium in minerals and rocks. Although a satisfactory method

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when the alkali metals are present at appreciable concentrations, accuracy deteriorates sharply as their concentrations decrease to low levels. The presence of serious error became apparent in a comparison of some chemical and spectrochemical determinations in chondritic meteorites (Ahrens, Pinson and Kearns, 1952) where the concentration of potassium is usually about 0·1%. At the much lower concentrations of potassium which are common in ultramafic rocks, errors in the chemical determinations are probably far greater. The presence of potassium in $CaCO_3$ used in the Lawrence-Smith fusion (see Groves, 1951, for example) is the probable source of error and although analysts frequently attempt to remove potassium by repeated water leaching of the $CaCO_3$, a significant proportion is likely to be retained (Hey, 1952) thereby causing a high result. As a consequence, virtually all chemical determinations of potassium in potassium-poor ultramafic rocks are wholly inaccurate or at best indicate an approximate magnitude. An attempt to apply a blank correction is rarely successful because the blank concentration is commonly many times greater than that in the unknown.

In our investigation a spectrochemical procedure has been developed and used. Although it is not as accurate as the most accurate spectrochemical methods and is also prone to some blank error (see below) it is believed that the determinations are reliable. A brief description of analytical procedure follows.

All determinations were made on a large Hilger Littrow spectrograph, using glass optics. A D.C. arc discharge (230 volts on open circuit and carrying 3 amps) excited the powdered specimens (each mixed with two parts of powdered carbon) in the cavity ($\frac{1}{8}$ in. ext. diam., $\frac{1}{16}$ in. int. diam. and $\frac{1}{4}$ in. depth) of a carbon anode. An 8-step rotating sector with a transmission factor of two served to provide a graded series of exposures during each analysis. Spectra were recorded on Eastman 1-L plates. Moving plate observations showed that the major proportion of each alkali metal distils within the first few seconds and that alkali metal volatilization is complete at from 10 to 30 seconds, depending on the total alkali metal concentration. Exposures were variable and were timed according to the length of the alkali metal period of volatilization.

Because of rapid volatilization, lines of the alkali metals emit their peak intensities during the first few seconds of exposure and as a consequence particular care must be taken to record the very first few seconds of arcing.

A low detection limit is usually attainable with the pair K7664·91A and K7698·98A. This limit is determined largely by the intensity of CN red emission. Such emission is virtually eliminated in the presence of a moderately high concentration of alkali metal vapour (see also comments below) in which case a detection limit of ~1 ppm may be reached. No attempt was made to add alkali metal salts in this investigation because of the danger of contamination; consequently CN emission was usually moderate and the detection limit was increased to about 10 ppm. Although useful, this detection limit was not wholly satisfactory because the concentration of potassium in many of the unknowns was at about this level.

Manipulation of electrodes with the fingers may cause contamination from perspiration. This is easily observable, particularly on hot days, and can be a source of very serious error when the potassium concentration in the sample is less than about 0·01% (100 ppm). (For detailed observations, see Holyk, 1952.) To avoid finger manipulation, a special stainless steel electrode loader (Holyk, 1952) was used. If, however, electrodes are inadvertently contaminated, potassium in the perspiration is easily removed by heating the loaded electrode to a red heat in a gas flame; potassium in the sample itself is not affected.

Serpentine arcs poorly, whether mixed with carbon or not, and is likely to blow out of the cavity shortly after the arc has struck. This is probably due to a rapid release of water vapour. A satisfactory burn may, however, be obtained by first removing water vapour from the specimen by heating the loaded electrode at a red heat for a few seconds in a gas burner flame.

Possible systematic error due to compositional differences between unknowns and standards

was reduced to a minimum by mixing a low potassium peridotite (No. 34; Quebec, Canada) with varying proportions of standard granite G-1 (Fairbairn *et al.*, 1951). The potassium concentration ranged from 0·0004% to 1% in these standards.

The reproducibility of the method is such that in a single arcing, potassium may usually be determined to within about 20% of its concentration when above ~0·003%. At lower concentrations closer to the detection limit, accuracy is poorer.

Experiments which have been carried out subsequent to the completion of this investigation show that in addition to the use of alkali metals, CN red emission may be effectively reduced by either, (a) use of a copper anode + carbon cathode (see Holyk, 1952) or, (b) flushing the discharge with helium vapour. It should therefore be possible to determine potassium accurately over the range of ~1 ppm to 30 ppm.

Selection of specimens

Fifty specimens of ultramafic rock were obtained from various sources. Seven from Dr. G. L. Davis of the Geophysical Laboratory are listed in Table 1 with P numbers as well as our numbers. Davis and Hess (1949) have discussed the Ra content of these rocks; their paper should be consulted for full petrographic descriptions. Prof. G. Kennedy (Harvard University) provided several specimens from southeast Alaska (see discussion by Kennedy and Walton, 1946) while Prof. H. W. Fairbairn (M.I.T.) and Dr. J. M. Black (British Columbia Department of Mines) supplied specimens from Russia and New Zealand, and British Columbia, respectively. Other specimens have been obtained from the Harvard and M.I.T. collections. Locality details and brief petrographic descriptions of each specimen are given in the Appendix. Dunite and serpentine are the commonest varieties in our suite of specimens.

Results

For the purpose of presenting the results, specimens will be subdivided in accordance with the classification of Davis and Hess (1949) as follows:

(1) *Ultramafic rocks of the basaltic magma suite*

These rocks are frequently associated with basic (gabbro) sheets and lopoliths (Skaergaard, Bushveld, Duluth, Stillwater, Sudbury, etc.) and are believed to have been formed by differentiation of a magma of basaltic composition. Twenty-seven specimens, three of anorthosite, have been analyzed.

The specimens from southeast Alaska are from a dunite-pyroxenite-gabbro suite (Kennedy and Walton, 1946). Unlike ultramafic rocks from other areas (Skaergaard, Bushveld, Duluth, etc.) which comprise a small proportion of the total volume, these ultramafics approximately equal the abundance of the gabbro. As a consequence they may not rightfully belong to this group.

(2) *Ultramafic rocks of primary peridotitic suite*

Rocks coming under this classification are those which are commonly associated with orogenic belts and which occur as isolated bodies—the Alpine peridotites of Benson (1926). These rocks may be representatives of a primary peridotitic magma. They are comparatively abundant and, because significant quantities of deep-lying crystal and mantle material may be of their composition, they are of

Table 1. *Potassium content of various ultramfic rocks*

Rocks of basaltic magma suite or of uncertain classification

Sample No.	*Rock type*	*Location*	% *K*
3	Dunite	S.E. Alaska	0·002
11	Dunite portion (cf. 8)	S.E. Alaska	≤0·001
21	Dunite	S.E. Alaska	≤0·001
29	Dunite	S.E. Alaska	≤0·001
5	Lherzolite	Sudbrook Park, Md.	0·035
7	Peridotite	S.E. Alaska	0·004
9	Wehrlite	S.E. Alaska	0·009
12 (Sc 10)	Lherzolite	Baltimore County, Md.	0·034
15	Wehrlite	S.E. Alaska	0·002
18	Pyroxene-Olivine Rock	Duluth, Minn.	0·034
23	Mica Peridotite	Arkansas	>3·5
32	Cumberlandite	Rhode Island	0·005
35	Peridotite	Cortlandt Series, N.Y.	0·18
37	Wehrlite	West Point, N.Y.	0·16
6	Pyroxenite	S.E. Alaska	0·005
8	Pyroxene portion (cf. 11)	S.E. Alaska	≤0·001
13	Hypersthenite	Oakwood, Md.	0·006
17	Pyroxenite (Olivine bearing)	S.E. Alaska	0·006
20	Pyroxenite	S.E. Alaska	0·005
22	Mica Pyroxenite	S.E. Alaska	0·15
40	Pyroxenite, Biotite bearing	S.E. Alaska	>3·5
42	Pyroxenite	Rhodesia	0·008
49	Bronzitite	E. Side, Big Horn Mountains	0·011
45	Pyroxene	Merensky Reef, Transvaal	0·059
14	Anorthosite	Cartierville, P.Q.	0·23
26	Anorthosite	Split Rock, Minn.	0·25
43	Anorthosite	St. Jerome, P.Q.	0·25
	Ultramafic rocks of primary peridotite suite		
1	Serpentinite	Thetford, P.Q.	≤0·001
2 (P141)	Serpentinite	Geiger's Quarry, Wash.	≤0·001
19	Serpentinite (grades into sample 34)	Thetford, P.Q.	≤0·001
25	Serpentinite	Bare Hill, Md.	≤0·001
27 (P318)	Serpentinite	Belvedere Mt., Vermont	≤0·001
39	Serpentinite	Saranovskoya, Russia	≤0·001
50	Serpentinite	New Caledonia	≤0·001
4 (P145)	Dunite	Twin Sisters Mt., Wash.	≤0·001
10 (P320)	Dunite	Thetford, P.Q.	≤0·001
28 (P391)	Dunite	Addie, N.C.	≤0·001
31 (P140)	Dunite	Balsam Gap, N.C.	≤0·001
33	Dunite	Nelson, N.Z.	≤0·001
38	Dunite	Nizni Taguil, Russia	≤0·001
46	Dunite	Nizni Taguil, Russia	0·002
51	Dunite	Dun Mt., N.Z.	≤0·001
52	Dunite	Krasny Urals Mine, Russia	≤0·001
16 (P369)	Websterite	Webster, N.C.	0·003
30	Saxonite	Riddle, Oregon	≤0·001
34	Peridotite	Thetford, P.Q.	≤0·001
41	Peridotite	Bakerville, N.C.	0·002
44	Peridotite	Black Lake, P.Q.	≤0·001
48	Lherzolite	Lac Lherz, Pyrenees	≤0·001
53	Peridotite	Atlin, British Columbia	≤0·001
54	Amphibole-Olivine Rock	Atlin, British Columbia	0·01
24	Pyroxenite	Webster, N.C.	≤0·001
	Secondary peridotite suite		
47	Hortonolite Dunite	Transvaal	<0·001

considerable interest. Twenty-five specimens have been analyzed: dunite and serpentine predominate.

(3) *Ultramafic rocks of the secondary peridotite suite*

Rocks from pipes and irregular intrusions. One specimen has been analyzed.

The potassium determinations of all specimens, classified as above, are given in Table 1.

Discussion

(1) *Abundance of potassium in ultramafic rocks*

No attempt will be made to review all previous chemical determinations in detail. Table 2 gives the average potassium content in a few ultramafic rocks as given by Daly (1933).

Table 2. Average potassium content of some ultramafic rocks after, Daly (1933)

	% K_2O
Lherzolite	0·21
Harzburgite and Saxonite	0·13
Bronzitite	0·11
Dunite	0·04

No average is given for serpentine, but Clarke and Washington (1924) list several determinations; these range from "none" to 0·16% K_2O.

The values given in Table 1 are in general far lower than those given in Table 2.

Twenty-one out of twenty-five specimens of dunite, serpentine and peridotite belonging to the "Alpine" type average at ~0·001% K. Higher concentrations are shown by one specimen of Russian dunite (0·002%), peridotite from Bakerville, North Carolina (0·002%), websterite from North Carolina (0·003%) and an amphibole-olivine rock from Atlin, British Columbia (0·01%). The average for all dunites and serpentines of the Alpine type is approximately 0·001%: this is the value that is used below in discussions on earth structure and heat contribution by K^{40}. It is 30–40 times less than Daly's average dunite and four times less than the approximate tentative value given by Ahrens, Pinson and Kearns (1952).

Dunites from the basaltic magma suite contain about the same concentration of potassium as those of the Alpine type. The potassium content of other ultramafic rocks of the basaltic magma suite appears, in general, to be considerably greater than that in dunite, even if varieties containing feldspar and/or mica are excluded. Those which contain feldspar and/or mica have a far greater potassium content. Biotite or plagioclase was detectable in seven out of ten specimens containing more than 0·01% K.

Each of the three specimens of anorthosite contains about 0·25% K, which is considerably lower than an average of 0·74% given by Daly (1933).

(2) *Heat production by K^{40}*

It is sometimes assumed that the earth's mantle is composed of material which has the composition of dunite: (Bullen, 1947, Chaps 12 and 13; Birch, 1951, p. 116, and Mason, 1952, p. 36). A recent interpretation (Birch, 1952) of seismic data does, however, not support a dunite mantle and it can be shown that the abundance data of potassium as given here can be used as chemical evidence to indicate that the mantle cannot have a *chemical* composition equivalent to that of pure dunite. In this respect one assumption is made, namely, that the earth's mantle and crust originated from primary cosmic material which had the chemical composition of the commonest silicate meteorite, chondrite. (There is chemical evidence that in certain respects the composition of earth and chondritic material are identical. Ahrens, Pinson and Kearns (1952) have shown that to within narrow limits the value of the ratio K/Rb in the earth is the same as that in meteorites and this may be taken to indicate that the abundance relationship of several other *lithophile* metals (Na, K, Li,* Al, Ca, Sr, Ba, Al, etc.) may be the same in terrestrial and extraterrestrial material.) For the purpose of calculation the following values will be used:

Mass of mantle + crust	4047×10^{24} g
Mass of mantle	4000×10^{24} g
Mass of crust	47×10^{24} g
Abundance of K in chondrites	0·09%† (Ahrens, Pinson and Kearns, 1952)
Abundance of K in dunite	~0·001% (this paper)
Abundance of K in crust	~1·8–2·6% (see discussion below)

It is difficult to assign an accurate value to the abundance of potassium in the crust. The value of 2·6% K given by Clark and Washington (1924) is often regarded as applying to the crust; actually it applies to surface and near-surface igneous rocks. Approximately the same value is obtained by taking two parts of average granite (3·4% K, Daly, 1933) and one part average basalt (~1·0% K). (The potassium abundance in average basalt may vary considerably, depending on how much weight is given to the two most common varieties, olivine basalt and tholeiite. For our purpose, however, a general magnitude only is required and the value of 1% should be satisfactory.) The proportion of basalt in the crust is likely to be greater than noted above and if 1 : 1 and 1 : 2 proportions of granite to basalt are taken, the potassium abundance is approximately 2·2 and 1·8%, respectively. In this discussion a range 1·8–2·6% is considered. The mass of potassium in the crust ranges therefore from 0·85 to $1{\cdot}2 \times 10^{24}$ g, and as the mass of potassium in primary undifferentiated mantle + crust of chondritic composition would be $4{\cdot}05 \times 10^{24}$ g, this leaves approximately 3×10^{24} g for mantle alone. If the mantle is assumed to contain 0·001% K, the mass of potassium is only $0{\cdot}04 \times 10^{24}$ g, a small fraction. The abundance of Rb, Na, Li and other elements in chondrites, granite, basalt and ultramafics may be used in the

* Because of the possibility of Li participating in thermonuclear reactions, this element may be omitted.

† This magnitude has been confirmed by Holyk (1952). Like Ahrens, Pinson and Kearns (1952), a spectrochemical method was used; different standards and a different analytical technique were, however, employed and the determination may therefore be regarded as a fairly independent check.

same way to show that the whole or a major proportion of the mantle cannot have the composition of pure dunite if it were originally of chondritic composition.

In order to give $\sim 1{\cdot}0 \times 10^{24}$ g potassium in the crust, 1000×10^{24} g of chondrite (0·09% K) would have to differentiate; this corresponds to about 25% of total original material. On this basis about 20–30% of the mantle could conceivably have the chemical composition of pure dunite. (Possible change of phase with depth (Birch, 1952) is not discussed.) The heat contribution by K^{40} in such dunitic material would probably be small compared with that generated by the U + Th series. On the basis of Davis' (1947) data the heat generated by the U + Th series in ultramafic rocks is of the magnitude of $0{\cdot}02 \times 10^{-6}$ cal/g/yr which may be compared with a value of only $0{\cdot}00025 \times 10^{-6}$ cal/g/yr generated by dunite containing 0·001% K.

Heat production by potassium in possible mantle material of chondritic composition is at present $\sim 0{\cdot}025 \times 10^{-6}$ cal/g/yr. This may be of the same magnitude or actually greater than that produced by the U + Th series. Accurate information is not yet available on the U + Th content of chondrites. Davis' (1950) values indicate that unlike potassium, the abundance of these two elements may be of about the same general magnitude in meteorites and dunite.

In the above calculations of heat production involving K^{40}, the following decay constants have been used: half-life, $1{\cdot}27 \pm 0{\cdot}1 \times 10^9$ years and $\lambda K/\lambda_\beta = 0{\cdot}135$ (Sawyer and Wiedenbeck, 1949); energies (Alburger, 1949, 1950 and 1951) $E = 1{\cdot}47$ Mev and $E_{max} = 1{\cdot}34$ Mev. A vast literature has grown around the decay of potassium and for a complete bibliography, see Birch (1951). It is considered that the above values are sufficiently reliable and accurate for this discussion and are the same as those used by Birch (1951) in his discussion of the importance of the radioactivity of K^{40} in geophysics.

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Appendix

Location and Brief Description of Samples

1. *Serpentinite* (M.I.T.) Bell Mine, Thetford, P.Q. A dull greenish-grey serpentine with a porcelain-like texture. Several grains of pyroxene up to 2 mm in size occur in the fine-grained groundmass.
2. *Serpentinite* (p. 141, Davis and Hess) Geiger's Quarry, Wash. For petrographic description see report by Davis and Hess (1949).
3. *Dunite* (43-AK-142, Kennedy) Blashke Islands, S.E. Alaska. A highly altered, black dunite cut by numerous veinlets of serpentine.
4. *Dunite* (p. 145, Davis and Hess) Twin Sisters Mtn., Whatcom, Wash. A massive, fresh, light greenish-grey dunite, coarse grained, contains traces of euhedral chromites.
5. *Lherzolite* (1316, M.I.T.) Sudbrook Park, Maryland. A fresh, dark greenish-brown rock in which crystals of pyroxene up to 10 mm in length can be observed. Light grey crystals of plagioclase are scattered throughout and form about 5% of the rock.
6. *Pyroxenite* (43-AK-478, Kennedy) Mt. Burnett, S.E. Alaska. A fresh specimen of massive, coarse grained pyroxene.
7. *Dunite* (43-AK-530, Kennedy) Mt. Burnett, S.E. Alaska. A medium grained, light brown, granular specimen consisting of olivine grains and about 5% disseminated magnetite.
8. *Pyroxene* (43-AK-435, Kennedy) Mt. Burnett, S.E. Alaska. The pyroxene portion of a dunite dike containing large crystals of pyroxene (see sample 11).
9. *Wehrlite* (43-AK-74, Kennedy) Blashke Islands, S.E. Alaska. A non-homogeneous specimen consisting of coarse grained pyroxene and fine grained, brown olivine. Specimen is partly weathered.
10. *Serpentinized Dunite* (p. 320, Davis and Hess) King's Mine, Thetford, P.Q. Consists of granular olivine intersected by a network of serpentine veinlets. Serpentine forms about half of specimen.
11. *Dunite* (43-AK-435, Kennedy) Mt. Burnett, S.E. Alaska. Dunite portion of dunite dike containing large crystals of pyroxene (see sample 8).
12. *Lherzolite* (Sc10, M.I.T.) Baltimore, Md. Rock contains about 5% plagioclase crystals. Specimen appears similar to number 5.
13. *Hypersthenite* (1306, M.I.T.) Oakwood, Md. A granular pyroxenite with grains up to 5 mm in size. Interstices are occupied by plagioclase which forms about 5% of rock. Specimen appears partly weathered.
14. *Anorthosite* (M.I.T.) Cartierville, P.Q. A fresh, massive, medium grained rock consisting of plagioclase and trace of sulphides.

15. *Wehrlite* (43-Ak-112, Kennedy) Blashke Islands, S.E. Alaska. A medium grained rock composed mainly of dark brown pyroxene grains. A few grains of bluish-green olivine are present. Rock contains large phenocrysts of clear, green diopside.
16. *Websterite* (p. 369, Davis and Hess) Webster, N.C. A medium grained, granular, somewhat friable rock consisting of light brown pyroxene and bright green olivine in approximately equal amounts. Fresh appearance.
17. *Pyroxenite* (43-AK-75, Kennedy) Blashke Islands, S.E. Alaska. Specimen consists almost entirely of coarse grained diopside with few crystals of olivine.
18. *Pyroxene-Olivine Rock* (2409, M.I.T.) 4 miles N.W. of Duluth, Minn. A coarse grained rock consisting of pyroxene crystals and serpentine. A few flakes of biotite are present.
19. *Serpentinite* (5770, M.I.T.) Thetford, P.Q. A dark green, dense serpentine, described as grading into altered peridotite 5771, sample 44.
20. *Pyroxenite* (43-AK-107, Kennedy) Blashke Islands, S.E. Alaska. From a pyroxenite dike. Consists essentially of pyroxene grains up to 15 mm in size with some black specks believed to be serpentine. Fresh appearance.
21. *Dunite* (43-AK-525, Kennedy) Mt. Burnett, S.E. Alaska. Specimen consists of fresh, fine grained, light greyish-brown olivine.
22. *Mica Pyroxenite* (43-AK-452, Kennedy) Mt. Burnett, S.E. Alaska. A medium grained, granular, friable rock consisting of pyroxene and about 2% biotite flakes.
23. *Mica Augite Peridotite* (S49, M.I.T.) Murfreesboro, Ark. A dull, greenish-brown, altered rock containing about 2% biotite.
24. *Pyroxenite* (S57, M.I.T.) Webster, N.C. Consists of fresh, coarse grained orthorhombic pyroxene. Contains about 1% bright green specks which may be olivine.
25. *Serpentinite* (1319, M.I.T.) Bare Hill, Md. A dull, yellowish-green serpentine, somewhat granular in appearance. Contains traces of magnetite.
26. *Anorthosite* (S44, M.I.T.) Split Rock, Minn. Massive, coarse grained rock consisting of light grey plagioclase. Very fresh appearance.
27. *Serpentine* (p. 318, Davis and Hess) Belvedere Mts., Vt. Hess and Davis report rock as being 87% serpentinized.
28. *Dunite* (p. 391, Hess and Davis) Addie, N.C. A fresh, fine grained rock consisting of polygonal olivine grains and about 2% chromite.
29. *Dunite* (43-AK-47, Kennedy) Blashke Islands, S.E. Alaska. Very fine grained, partly weathered olivine, crisscrossed with iron stained fractures.
30. *Saxonite* (M.I.T.) Riddle, Oregon. Consists of olivine and enstatite.
31. *Dunite* (p. 140, Davis and Hess) Balsam Gap, N.C. A sugary textured, medium grained, light green rock consisting of olivine and minor chromite.
32. *Cumberlandite* (4791, Harvard) Cumberland, R.I. Specimen consists of serpentine and olivine which has been replaced by about 40% magnetite.
33. *Dunite* (867, Harvard) Nelson, New Zealand. Massive light yellowish-green olivine, very fresh in appearance. Contains 1% disseminated chromite.
34. *Peridotite* (6464, M.I.T.) Dump of Asbestos Corporation Mine, Thetford, P.Q. A fresh, greenish-grey rock in which about 10% pyroxene grains occur in a finer grained groundmass.
35. *Peridotite* (1170, Harvard) Cortlandt Series, Montrose Pt., N.Y. A black, medium grained rock consisting essentially of pyroxene. Contains traces of pyrrhotite.
37. *Wehrlite* (4955, M.I.T.) Dickerson Hill, Westpoint, N.Y. Fresh, medium grained rock consisting of pyroxene and olivine. A few specks of biotite are present.
38. *Dunite* (10194-11, M.I.T.) Nizhni Taguil, Russia. A partly serpentinized fine grained dunite containing 1% chromite.
39. *Serpentinite* (9216-10, M.I.T.) Saranovskoya, Russia. A massive, dark green serpentine, somewhat granular, contains 5% chromite.
40. *Mica Pyroxenite* (43-AK-437, Kennedy) Mt. Burnett, S.E. Alaska. A friable specimen consisting of equal amounts of medium grained pyroxene and biotite.
41. *Peridotite* (3131, Harvard) Bakerville, Mitchell County, N.C. A fine grained, somewhat weathered rock, consisting of granular olivine and about 5% pyroxene.
42. *Pyroxenite* (1949, M.I.T.) Rhodesia. Very fresh, medium grained, orthorhombic pyroxene.

43. *Anorthosite* (4006, Harvard) St. Jerome, P.Q. A fresh specimen of protoclastic plagioclase containing black streaks of ilmenite.
44. *Peridotite* (5771, M.I.T.) Black Lake, P.Q. Specimen is described as a typical specimen of Black Lake peridotite. A fine grained rock containing about 10% pyroxene grains up to 3 mm in size, very fresh appearance.
45. *Pyroxenite* (M.I.T.) Lydenburg District, Merensky Reef, Transvaal. A medium grained rock consisting of pyroxene and 5% plagioclase in interstices.
46. *Dunite* (10194, M.I.T.) Nizhni Taguil, Russia. Very fresh specimen of fine grained, dark green olivine, contains 1% chromite.
47. *Hortonolite Dunite* (M.I.T.) Lydenburg District, Transvaal. Fresh, coarse grained olivine, dark brown colour, sub-metallic lustre.
48. *Lherzolite* (4003d, Harvard) Lac Lherz, Pyrenees. Massive fine grained, fresh rock consisting of olivine and pyroxene with traces of magnetite.
49. *Bronzitite* (20580, Harvard) E. Side Bighorn Mts., on Buffalo-Tensleep road. Consists of fresh, coarse grained pyroxene.
50. *Serpentinite* (9171, M.I.T.) Fontoche Mine, New Caledonia. A dull green serpentine in which several grains of pyroxene are present.
51. *Dunite* (Fairbairn) Dun Mountain, N.Z. Consists of yellowish-green, glassy, medium grained olivine; contains 1% chromite. Specimen is portion of drill core.
52. *Dunite* (Fairbairn) Krasny Ural Mine, Urals, Russia. Fresh mottled green olivine, contains about 5% chromite in disseminated patches.
53. *Peridotite* (Black) Atlin, B.C. Appears to be serpentine in hand specimen. Thin section shows serpentinized olivine with minor amphibole.
54. *Amphibole-Olivine Rock* (Black) Atlin, B.C. Hand specimen consists essentially of radially fibrous amphibole.

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The abundances of Li, Sc, Sr, Ba and Zr in chondrites and some ultramafic rocks*

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ABSTRACT

Quantitative spectrochemical determinations of Li, Sc, Sr, Ba and Zr in 21 specimens of chondrite, 7 other silicate meteorites and 13 ultramafic rocks are presented and discussed. Abundances in chondrites have been determined as: Li (2·7 ppm), Sc (6 ppm), Sr (11 ppm), Ba (8 ppm) and Zr (33 ppm). Each element shows a high degree of uniformity of abundance; distribution is possibly *lognormal*.

β-activity of Rb^{87} is calculated to generate ~13% of total Sr^{87} in chondrites.

Introduction

An earlier communication (Ahrens, Pinson and Kearns, 1952) on meteorites discussed the abundance and association of Rb and K in chondrites and common igneous rocks. This second paper discusses the abundances of Li, Sc, Sr, Ba and Zr in the same meteorites (21 chondrites plus a few other silicate meteorites) and some ultramafic rocks.

Although one principal object of these investigations is an attempt to determine the cosmic abundance of some rarer elements as reliably as possible, almost equal emphasis is placed on the determination of the degree of uniformity of abundance of elements in chondrites. Many of the earlier workers who investigated the rarer elements either analyzed a very small number of specimens (sometimes one or two) or a composite, and often used approximate procedures; as a result nothing could be concluded about uniformity of abundance. Close similarity in composition—at least with respect to lithophile elements both common and rare—becomes strikingly evident when the spectra of a suite of chondrites are examined.

Analytical Procedures

Each element was determined spectrochemically, using a D.C. arc. Metal was extracted from the meteorites prior to their analysis. Although Li, K and Rb possess similar spectroscopic properties, Li could not be determined with K and Rb and reported earlier (Ahrens, Pinson and Kearns, 1952). $\frac{3}{16}$ in. carbon electrodes were used for K and Rb; these cause excessively intense emission from Li 6707 and consequently re-arcing in a smaller ($\frac{1}{8}$ in.) electrode was necessary. The general procedure for all alkali metals is otherwise the same: each specimen is arced until the main alkali metal phase of distillation ceases. Sc, Sr, Ba and Zr were determined in a separate operation. For an outline of procedures see Ahrens (1951); details are given by Pinson (1951) and will be published later.

In order to reduce systematic error to a minimum, standards were prepared by mixing either of the standard rocks granite G-1 and diabase W-1 (Fairbairn *et al.*, 1951) with varying proportions of a meteorite or (Li only) a lithium-poor peridotite.

* Part of this research has been supported by the Office of Naval Research, Washington, and part is from a Ph.D. thesis by W. H. Pinson.

Five spectrochemists have determined each element in G-1 and W-1; in addition one chemist has determined Sr, Ba and Zr. The recommended values, usually the arithmetic means, for each standard rock, are:

W-1	—35 ppm Sc, 290 ppm Sr and 290 ppm Ba
G-1	—200 ppm Zr
G-1 + W-1 (1 : 1 mixture)	—22 ppm Li

Fig. 1. shows a typical addition method plot. The example is that of lithium. 1 : 2, 1 : 4, 1 : 8 and 1 : 16 mixtures of a 1 : 1 G-1, W-1 mixture (22 ppm Li) with a perioditite (Quebec,

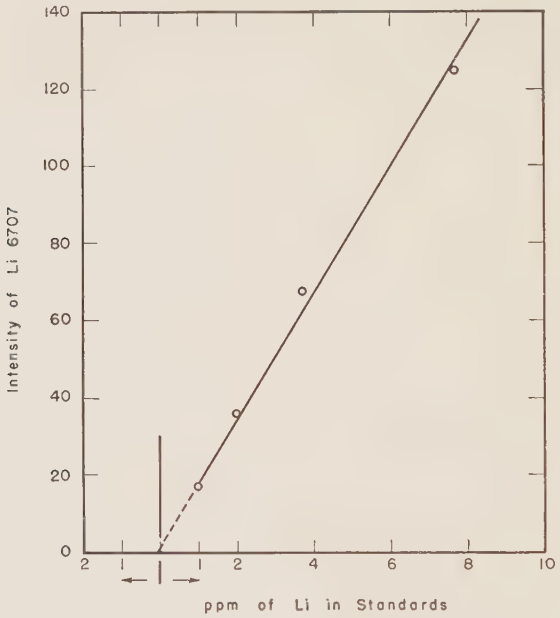

Fig. 1. *Addition plot for the determination of Li*

Ontario) low in lithium were used to obtain the addition plot (see for example, Ahrens, 1950) in Fig. 1. Extrapolation, as indicated, gives a value of approximately 0·15 ppm Li in the peridotite. A working curve may be prepared from Fig. 1 in the usual way. The same general procedure was employed for the determination of Sc, Sr, Ba and Zr. The precision (reproducibility) of each determination is such that when made in triplicate, two thirds of the determinations should be within 10% of the mean. No attempt was made to improve accuracy by internal standardization. It is believed that systematic error is at an insignificant minimum because standards and unknowns have similar mineralogy; ferromagnesians predominate in all specimens. Error in the assumed concentration (see above) of each constituent in W-1 and G-1 cannot, however, be overlooked; at the very worst, such an error could be −50% or +100%, but it should be much less, probably within −20% and +25%.

Analytical Results

All determinations are given in Tables 1 (a), (b) and (c). For the sake of comparison, values for Rb and K (Ahrens, Pinson and Kearns, 1952) are included.

Table 1 (*a*). *Li, Sc, Sr, Ba, Zr, K and Rb in chondrite specimens*

	Li (*ppm*)	Sc (*ppm*)	Sr (*ppm*)	Ba (*ppm*)	Zr (*ppm*)	K (%)	Rb (*ppm*)
Homestead[1]	2	10	18	11	45	0·11	12
Rancomé	2	4·5	7	7	22	0·13	14
Hayes Center	1·7	6	11	32[2]	46	0·07	6
Waconda	2	6	11	7	28	0·09	10
Assun	2·6	6·5	12	8	27	0·10	11
Holbrook	3·3	8·5	13	9	28	0·08	8
Bjurbole	2·7	6	11	8	47	0·10	9
Pultusk	3·6	6	10	7	32	0·06	5
Forest City	2·7	7·5	15	9	39	0·05	6
Hessle	2·8	8	12	7	24	0·08	6
Kernouve	—	6	11	6	24	0·09	7
Barratta	3·1	4·5	9	7	28	0·12	13
Mocs	2·1	5	9	7	29	0·11	10
Tennasilon	3·7	6	11	10	26	0·10	8
Monroe	3·2	4·5	12	5	37	0·07	7
Long Island	3·7	6	12	100[2]	28	0·06	10
Beaver Creek	—	6	7	5	23	0·08	6
Lumpkin	3·0	6	8	6	76[2]	0·06	7
Cangas de Onis	3·3	6	9	5	24	0·08	8
Estacado	3·0	6	9	6	25	0·07	6
Warrentown	~1·0	5	7	5	28	0·06	6
Average	2·7	6	11	8	33	0·09	9
Relative deviation (%)	26%	16%	20%	23%	23%	27%	29%

[1] Refer to Ahrens, Pinson and Kearns (1952) for descriptive details.
[2] Omitted from calculation of mean.

Table 1 (*b*). *Sc, Sr, Ba and Zr in other silicate meteorites*

	Sc (*ppm*)	Sr (*ppm*)	Ba (*ppm*)	Zr (*ppm*)
Pallasite olivine	<1	1	7	<1
Chladnite, Johnstown	14	3	5	30
Carbonaceous chondrite, Orgueil	4	<1	<1	<1
Carbonaceous nodule, Hessle	<1	10	8	30
Tektite, Annam, Indo China	<1	85	300	200
Tektite, Cambodia, Indo China	<1	100	320	200
Tektite, P.I.	<1	100	420	200

Table 1 (*c*). *Li, Sc, Sr, Ba and Zr in some ultramafic rocks*

		Li (*ppm*)	Sc (*ppm*)	Sr (*ppm*)	Ba (*ppm*)	Zr (*ppm*)
*P140	Dunite, Balsam Gap, N.C.	<0·3	7	~2	7	40
P145	Dunite, Twin Sisters Mt., Whatcon, Wash.	<0·3	9	<1	7	30
P320	Dunite (serpentinized) Kings Mine, Thetford, P.Q.	<0·3	10	<1	5	30
P391	Dunite, Addie, N.C.	<0·3	5	~2	5·5	30
P141	Serpentine, Geiger's Quarry, Wash.	<0·3	9	~1	8	20
P318	Serpentine, Belvedere Mt., Vt.	<0·3	6	<1	5	<2
P369	Websterite, Webster, N.C.	<0·3	50	~2	5·5	10
S-57	Pyroxenite, Webster, N.C.	—	13	~2	13	30
—	Saxonite, Riddle, Oregon	—	13	?	<1	~3
Sc-10	Lherzolite, Baltimore, Md.	—	20	20	60	50
—	Kimberlite, S. Afr.	—	15	280	700	100
S-49	Mica augite peridotite, Murfreesboro, Ark.	—	8	130	1000	400
S-44	Anorthosite, Split Rock, Minn.	—	<2?	290	80	<2

* Refer to G. L. Davis and H. H. Hess (Amer. J. Sci., 1949, **247**, 856) for descriptive details of P series.

Discussion

Lithium

The only earlier determinations of lithium in chondrites are those given by Strock (1936). These values (Table 2) have served as the basis for all earlier abundance discussions and calculations (Goldschmidt, 1937; Rankama and Sahama, 1949; Brown, 1949; Urey, 1952). Strock employed a spectrochemical procedure and

Table 2. *Li in two specimens of chondrite* (Strock, 1936)

	Li (*ppm*)
Knyahinya, Hungary	5
Aztek, Navajo, Arizona (silicates only)	2·5
Average	3·5

his values agree well in magnitude with those given here which average at 2·7 ppm. The relative deviation (equivalent to standard deviation expressed as per cent, coefficient of variation or the per cent spread) is about 26%.

The low concentration of lithium in mica poor ultramafics (Table 1 (c)) contrasts sharply with its abundance in chondrites where it is enriched by a factor of $\times 10$–20 or more. (Such a relationship is similar to that for K and Rb reported by Ahrens, Pinson and Kearns, 1952.) This does not agree with Strock (1936,) who reported Li concentrations in ultramafic rocks closely similar to those in chondrites. Sahama (1945) reported extremely low Li concentrations in three specimens of ultramafic rock (one olivine-rock, and two serpentines), namely, 1·5, 0·5 and $<0{\cdot}5$ ppm, Li, respectively.

Scandium

A cosmic abundance vs. Z plot (see Goldschmidt, 1937 Rankama and Sahama, 1949, for example) shows a conspicuous minimum at scandium (Z = 21). The possibility that this might be due to some significant analytical error prompted our investigation on the cosmic abundance of scandium. Goldschmidt and Peters (1931) and I. Noddack (1935) report abundances of 5 and 6 ppm, respectively of Sc in meteorites; abundance plots are usually based on the use of these measurements.

The values in Table 1 (a) are almost identical and average at 6 ppm; the relative deviation calculates at 16%. Because of such close agreement one may conclude that the conspicuous abundance minimum is real and not due to analytical error.

The *dominant* isotopes of odd Z elements which precede Sc have a neutron excess (N–Z) of one. Sc^{45} has three, whereas dominant isotopes which follow scandium have a neutron excess of 5. In this sense, Sc^{45} is a transition nucleus and it is of interest to note that other transition elements in this sense, namely, gallium and possibly rhodium are also conspicuously rare. This topic will be discussed in greater detail elsewhere by one of us (A).

The ability of Sc^{3+} ($r = 0{\cdot}81$ Å) to replace Fe^{2+} ($r = 0{\cdot}74$ Å) and Mg^{2+} ($r = 0{\cdot}66$ Å) in certain ferromagnesians, notably pyroxene and biotite, was demonstrated by Goldschmidt and Peters (1931). Wager and Mitchell (1951) have subsequently emphasized the fact that such replacement is very slight, however, in olivine. See also Sahama (1945). In this respect, the Sc concentration in the limited number of non-chondritic meteorites is of interest: olivine from pallasite shows the lowest concentration (<1 ppm) whereas the Johnstown chladnite, composed almost wholly of bronzite, has the highest concentration (14 ppm).

The concentration of Sc in dunite and serpentine (range, 5 to 10 ppm; av., 8 ppm) is very similar to that found in the chondrites. Most of the pyroxene-bearing varieties of ultramafic rock show higher concentrations and a maximum (50 ppm) was found in websterite from North Carolina.

Strontium

The cosmic abundance values of Sr given by recent authors (Goldschmidt, etc.) are all based on the x-ray spectrographic determinations of von Hevesy and Würstlin (1934a) given in Table 3. Two of our determinations are given for comparison.

The average (23 ppm) in Table 3 is about twice our value of 11 ppm. The large spread ($\times 5$) of values given by von Hevesy and Würstlin is not consistent with the comparatively small relative deviation of 20% found in our observations. If the two highest values (Tabory and Karoonda) are omitted, the Table 3 average reduces to 15 ppm, close to our value.

Table 3. Sr in chondrites as determined by von Hevesy *and* Würstlin (1934a)

Meteorite	Sr (*ppm*)	
	(v.H. *and* W.)	(*This paper*)
Waconda, Kansas	~10*	9
Cuanta, Spain	~10	—
Pultusk, Poland	~20	7
Vigarvano, Piave, Italy	~20	—
Tabory, Russia	~30	—
Karoonda, South Australia	~50	—
Average	23	

* All meteorite values listed by von Hevesy and Würstlin have the approximate sign, which, however, is absent from their rock values. The low Sr concentrations in meteorites are presumably near the detection limit of their x-ray spectrographic method.

The abundance of Sr in pallasite, chladnite, serpentine and dunite is considerably less than in chondrites and is frequently of the magnitude of 1–2 ppm.

The β activity of Rb^{87} must have contributed some proportion of the total strontium in chondrites. For the purpose of calculation, $t\ (Rb^{87}) = 6{\cdot}0 \times 10^{10}$ years (Sawyer and Macgregor, 1952) and the age magnitude of chondrites,

Table 4. Calculated proportions (approximate) of radiogenic Sr^{87} in chondrites and igneous rocks

	Total Sr (*ppm*)	*Total* Rb (*ppm*)	*Radiogenic* Sr^{87} *generated* (*ppm*)	*Proportion of total* Sr (%)	*Proportion of* Sr^{87} (%)
Chondrites	11	9	0·1	1	13
Basalt	300	110	1	0·35	5
Granite	180	520	5	2·8	40
Igneous rocks* (2 gr : 1 basalt)	220	350	4	2·0	30

* Not equivalent to crust. Refers to surface and near-surface igneous rocks and hence makes these determinations comparable to Clarke and Washington's data which approximate to 2 parts granite and 1 of basalt.

$3{\cdot}5 \times 10^9$ years. Table 4 gives calculated proportions of radiogenic Sr^{87} in chondrites and also, for the sake of comparison, terrestrial igneous rocks: their oldest age has been assumed to be equal to that of the chondrites. Abundances of Rb and Sr in chondrites are from this paper. Rb in granite and basalt is from AHRENS, PINSON and KEARNS (1952) and Sr in granite and basalt is based in part on determinations given by FAIRBAIRN, AHRENS and GORFINKLE (1953) and unpublished data.

Barium

All cosmic abundance values given by recent authors (GOLDSCHMIDT, etc.) are based on the determinations made by VON ENGELHARDT (1936) and given in Table 5; values in this paper are given for comparison.

Table 5. Determinations of Ba in meteorites by VON ENGELHARDT (1936)

Meteorite	Ba (*ppm*)	
	VON E.	*This paper*
Eucrite; Stannern, Czechoslovakia	48	—
Eucrite; Juvinas, France	10–30	—
Chondrite; L'Aigle, France	3–10	—
Chondrite; Holbrook, Arizona	3–10	9
Chondrite; Hungary	1–3	—
Chondrite; Erx Uben, Saxony	1–3	—
Chondrite; Barbotan, France	1–3	—
Chondrite; Chautonnay, France	1–3	—
Chondrite; Avilez, Mexico	<1	—
Chondrite; Bjurbole, Finland	<1	8
Chondrite; Pultusk, Poland	n.dt.	7

GOLDSCHMIDT used the average (7 ppm) for all meteorites (eucrites and chondrites) as the cosmic abundance of Ba. Abundance values given by RANKAMA and SAHAMA (1949) and BROWN (1949) were essentially based on GOLDSCHMIDT'S average. UREY (1952), however, took into account the preponderance of chondritic meteorites, omitted the eucrite values and recalculated the average as 3 ppm.

The average given in this paper (8 ppm) is nearly three times as great. The reason for the discrepancy is difficult to find: one direct comparison (Holbrook) is apparently in agreement, whereas the other two (Bjurbole and Pultusk) differ by a factor of eight or more. The range (3–10 to <1 ppm) found by VON ENGELHARDT is not consistent with the comparatively small relative deviation of 23% found in our determinations.

Unlike strontium, the barium concentration in dunite and serpentine appears to be about the same as in the chondrites. There appears to be no obvious reason why the Ba/Sr ratio should be so high in dunite and serpentine. Olivine from

pallasite shows the same relationship. These observations accord with those of Sahama (1945) who reported the following values in Finnish ultramafics.

	Ba (ppm)	Sr (ppm)
Serpentine, Kittilä	30	<10
Serpentine, Sodankylä	<30	<10
Olivine rock, Salla	60	10

The barium concentration is greater than that of strontium in each specimen.

Zirconium

Recent (Goldschmidt, etc.) cosmic abundance values are all based on the x-ray spectrographic determinations of von Hevesy and Würstlin (1934b) given in Table 6. Two of our determinations are given for comparison.

Table 6. *Zr in stony meteorites, after* von Hevesy *and* Würstlin (1946b)

	Zr (*ppm*)	
	von H. *and* W.	*This paper*
Vigavano, Italy	~30	—
Karoonda, South Australia	~30	—
Pultusk, Poland	~40	32
Tabory, Russia	~80	—
Cuenta, Spain	150	—
Waconda	160	28

Von Hevesy and Würstlin's average is 80 ppm, ×2·5 our value of 33 ppm. Their average reduces to 45 ppm if the highest values (Cuenta and Waconda) are omitted. Agreement is close on the Pultusk specimen, but in the Waconda specimen their value is ×5 greater than ours. The determinations of von Hevesy and Würstlin range from 30 to 160 ppm (a factor of five) and as in the examples of Sr and Ba, it is difficult to reconcile such large variations with the moderately small relative deviation (23%) reported here for zirconium.

All specimens of dunite and serpentine (Belvedere Mt. specimen excepted) show concentrations of Zr very similar to those found in the chondrites.

Degree of uniformity of abundance

A statistical examination by Brown and Patterson (1947) of published determinations of Si, Mg, Fe, Al, Ca, Na, Ti, Ni, Cr, Mn, K and Co in all stones showed that the degree of uniformity of abundance decreased sharply with decrease in abundance. These authors felt that although some of the observed spread could be attributed to analytical error, most did actually occur. The range in scatter, expressed as a relative deviation was from about 10% for Si, the most abundant element (22% by weight) to about 170% for Co, the least abundant element (0·02% by weight). It was concluded also that very large numbers of stones would have to be analyzed in order to obtain reasonably accurate abundance values for

rarer elements. Contrary conclusions are reached when using the observations in this paper. Each constituent investigated (Li, Rb, K, Sc, Sr, Ba and Zr) shows a very high degree of uniformity of abundance.

The calculated range of relative deviations is from 15 to 30% (Table 1) and is independent of concentration. Actual scatter is undoubtedly somewhat less, because of a significant contribution (perhaps one half) from spectrographic error, and may be equivalent in magnitude to that of silicon. A visual inspection of our spectrographic plates indicates that a similar degree of uniformity of composition holds for common lithophile elements: this will be a subject of further study.

The high degree of uniformity of abundance of all lithophile elements in chondrites may be contrasted with specific rock types, where scatter is invariably far greater. Compare, for example, the frequency distribution diagram for several elements in diabase (Fairbairn, Ahrens and Gorfinkle, 1953) with the reported relative deviations given here.

It must be emphasized at once that whereas Brown and Patterson's conclusions are based on determinations of a wide variety of elements (some capable of participating in silicate, sulphide and metal phases) in various types of meteorites, ours are confined to lithophile elements in chondrites. Nevertheless, it is highly probable that much of the apparent scatter—sometimes a dominant proportion—is due to analytical error. Thus, for example, Co shows an apparent relative deviation of some 170% whereas chemically similar Fe shows a relative deviation of only 30%. There is little doubt that much of the apparent scatter shown by Co at a magnitude of 0·02% is due to analytical error at such a low concentration, as compared with the accuracy with which Fe is determined at much higher concentrations.

Statistical calculations of scatter are usually based on an assumed normal distribution of observations about a mean. Many examples are known, however, of decidedly abnormal distributions; a pertinent example is that of the geochemical distribution of elements. Extensive data, some published (see frequency distribution diagrams by Ahrens and Gorfinkle (1950) and Fairbairn, Ahrens and Gorfinkle (1953) and some as yet unpublished, show that the distribution of the concentration of an element about its mean concentration in a specific rock type is not normal but lognormal, or nearly so. As a result it is quite possible that the nature of the distribution of lithophile elements in chondrites is similar. The assumption of a lognormal distribution removes the difficulty of predicting negative values. In the above example of cobalt in meteorites, a relative deviation of 170% predicts that a significant proportion of all meteorites will have concentrations less than 0% Co (−100%), which is completely unreal. The calculated relative deviations given in Table 1 assume a normal distribution. As the dispersion is not particularly great, however, no serious distortion arises, although a more rigorous statement of distribution of concentration could probably be made on the basis of assumed lognormal distribution.

The remarkable degree of uniformity of abundance shown by Li, K, Rb, Sc, Sr, Ba, Zr and probably other elements in chondrites, supports their common origin in space and time.

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SYMPOSIUM ON THE ORIGIN OF METEORITES AT M.I.T.

WEDNESDAY, 30th DECEMBER, 1953

To be held at the American Academy of Arts and Sciences. Joint session of A.A.A.S. Section D with Sections E and B; arranged by H. H. UHLIG, Massachusetts Institute of Technology and F. L. WHIPPLE, Harvard Observatory.

9.00 a.m. H. H. UHLIG, Massachusetts Institute of Technology, *Presiding*

1. **On the Loss of Volatiles from Meteorites.** H. C. UREY, University of Chicago (30 min.).
2. **Age of Meteorites.** F. PANETH, University of Durham, England (15 min.).
3. **Paths, Velocities, and Orbits of Detonating and Stone-dropping Meteors.** C. C. WYLIE, University of Iowa (30 min.).
4. **Origin and Nature of Photographic Meteoroids.** F. L. WHIPPLE, Harvard Observatory (30 min.).
5. **Comment Relative to the Meteorite Pitting Phenomenon.** R. N. THOMAS, Harvard Observatory (15 min.).
6. **The Density and Distribution of Meteroritic Iron.** E. P. HENDERSON and S. H. PERRY, U.S. National Museum (30 min.).
7. **Distribution of Trace Elements in Iron Meteorites.** HARRISON BROWN, California Institute of Technology (30 min.).

1.30 p.m. F. L. WHIPPLE, Harvard Observatory, *Presiding*

8. **Contribution of Metallurgy to the Origin of Meteorites.** H. H. UHLIG, M.I.T. (30 min.).
9. **The Scattered Planet Hypothesis of the Origin of Meteorites.** W. H. PINSON, M.I.T. (30 min.).
10. **The Possible Occurrence of Nickel-free Iron Meteorites.** H. H. NININGER, American Meteorite Museum (30 min.).
11. **Cosmical Changes in Meteorites as a Clue to their Origin.** WALTER WAHL, Soc. Scientiarum Fen., Helsingfors, Finland (15 min.).
12. **Structure, Composition, and Probable Origin of Chondrites in Stony Meteorites.** S. K. ROY, Chicago Natural History Museum (30 min.).
13. **The Composition and Origin of Meteorites.** HARMON CRAIG, University of Chicago (30 min.).
14. **The Isotopic Composition of Hydrogen in Iron Meteorites and of Hydrogen and Carbon in Carbonaceous Chondrites.** GEORGE EDWARDS and GIOVANNI BOATO, University of Chicago (30 min.).
15. **Meteorites and Cosmic Rays.** S. F. SINGER, University of Maryland (30 min.).

8.00 p.m. BART BOK, Harvard Observatory, *Presiding*

16. **Summary Remarks.** HARRISON BROWN, California Institute of Technology (20 min.).
17. **Origin of Meteorites.** H. C. UREY, University of Chicago (40 min.).

D IN STACKS

DEEP-SEA RESEARCH

EDITORS

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